

PHOTOLUMINESCENCE DUE TO LOCALIZED CHARGE CARRIERS
IN SOME COMPOUND SEMICONDUCTORS

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Localized charge carriers in some semiconductor compounds are studied in this thesis using photoluminescence, (PL), optical detection of magnetic resonance, (ODMR), and by creating defects by diffusion. The results obtained are presented in the following papers:

- I Neutral (Cu-Li) Complexes in GaP: The $(\text{Cu-Li})_{\text{I}}$ bound exciton, at 2.306 eV, (Phys. Rev. B, March 15, 1985).
- II Neutral (Cu-Li) Complexes in GaP: The $(\text{Cu-Li})_{\text{III}}$ bound exciton, at 2.242 eV, (accepted for publication in Phys. Rev. B).
- III Neutral (Cu-Li) Complexes in GaP: The $(\text{Cu-Li})_{\text{V}}$ bound exciton, at 2.172 eV, (manuscript, to be submitted to Phys. Rev. B).
- IV ODMR Investigation of a Deep Li-related Complex in GaP, (manuscript).
- V ODMR Excitation Spectroscopy in GaP, (J. Phys. C17, 943 (1984)).
- VI Disorder-induced Anderson localization in $\text{GaAs}_{1-x}\text{P}_x$, (Sol. St. Comm. 52, 789 (1984)).
- VII Photoluminescence studies of localization effects induced by the fluctuating random alloy potential in indirect gap $\text{GaAs}_{1-x}\text{P}_x$, (manuscript, to be submitted to J. Phys. C).

INTRODUCTION

The understanding of the physics of semiconductors is expanding at a rapid rate. In the following a brief introduction to bound excitons and the features seen in photoluminescence will be given. There will also, as a background, be a small discussion about the materials studied.

EXPERIMENTAL TECHNIQUES

The experimental methods used in this work are based on photoluminescence and the objects studied are charge carriers bound to defects [1] or bound to alloy fluctuations [2, VI, VII]. A bound exciton is an electron- and a hole pair bound to a defect. The study of impurities in semiconductors via their bound excitons is a very powerful method, giving information on the atoms present in the impurity through isotope doping [3], and on the local arrangement of atoms by monitoring magnetic resonance via luminescence, a technique called optical detection of magnetic resonance, (ODMR) [4]. Photoluminescence, hereafter called luminescence, is well suited for the study of excitons. The sample is excited with a laser. If the energy of the photons from the laser is greater than the bandgap, free electrons and holes are created. These may be captured at a defect and form a bound exciton. Emission from this bound exciton can then be monitored, see Fig. 1.

In ODMR a micro-wave field and a magnetic field are applied to the sample, in addition to the exciting laser light. The situation for a triplet state, (which is often the case for excitons bound to complex defects in GaP), is illustrated in Fig. 2. At a certain magnetic field the micro-waves will cause transitions between the sublevels of the triplet. The sublevels usually have different luminescence efficiency. Inducing micro-wave transitions will then cause a change of the total luminescence intensity from the three

levels, which is subsequently detected. Many of the bound excitons studied in this thesis give ODMR signals from triplet states [I-V].

ELECTRONIC STATES

A defect in a semiconductor crystal breaks the translational symmetry of the crystal and it may create localized energy levels in the band-gap. Shallow donors and acceptors are examples of defects, which are important in semiconductor technology. A defect that is neutral in its ground state may have excited states in the band-gap. If a bonding electron in a neutral centre is excited, but the centre is not ionized, the resulting state is called a bound exciton [1]. A donor or an acceptor may have excited many-particle states which then are excitons bound to the donor or acceptor [1]. A bound exciton is a many-particle excitation and is not easily depicted by indicating an energy level in a one-particle energy band figure.

Group theory is a powerful tool in physics [5]. Because of the difficulty to derive the results of group theory in a few pages, it will be assumed that the reader has some knowledge of group theory. The notation will be as in reference 5, if the group does not include spin. If spin is included the notation of reference 6 will be used. This seems to be one of the widely used notations in exciton literature. Double groups will be denoted with a prime. T_d' is, for example, the double group of T_d .

If the reader only has a scant knowledge of group theory, the various symbols used like, A_1 , E , Γ_6 , can be seen merely as labels of possibly degenerate quantum states. Group theory efficiently tells if removal of a degeneracy among quantum states is expected in the presence of a perturbation.

GENERAL PROPERTIES OF GALLIUM PHOSPHIDE AND GALLIUM ARSENIDE PHOSPHIDE

Gallium phosphide (GaP) and gallium arsenide phosphide ($\text{GaAs}_{1-x}\text{P}_x$) are both members of the III-V family of semiconductors. They both have the zinc-blende crystal structure shown in Fig. 3. GaP is a material with an indirect bandgap of 2.35 eV [7]. The energy bandstructure is shown in Fig. 4 [8]. $\text{GaAs}_{1-x}\text{P}_x$ is an alloy and the bandstructure is dependent on the composition x . As and P are situated on the same sublattice but are distributed randomly. The random potential breaks the translational symmetry of the lattice and the concept of a band-structure does not strictly survive.

GALLIUM PHOSPHIDE

In Fig. 4 various high-symmetry points in the bandstructure of gallium phosphide are indicated. They can be compared with the points in Fig. 5 showing the Brillouin zone of the zincblende lattice. Feature of GaP is the occurrence of a camel's back structure (Fig. 6). The conduction band minima are not situated exactly at the zone boundary but are displaced about 8% inwards [1], a phenomenon called camel's back. The small effects arising from the camel's back will hereafter be neglected.

Under the point group T_d the conduction band minima transform as X_1 , if the origin of coordinates is taken on a phosphorus site. If the origin is on a gallium site they transform as X_3 [9]. The notation in Fig. 5 is for an origin on a P-site. As is shown in Fig. 4, the top of the valence band transforms as Γ_5 (including spin) under T_d . This band is split, by the spin-orbit (S-O) interaction, into a Γ_8 and a Γ_7 , where Γ_8 forms the top of the valence band (Fig. 7). A hole from the Γ_8 transforms as a $P_{3/2}$ atomic wave-function with $J=3/2$. If the hole is in the Γ_7 band it has $J=1/2$ and transforms as a $P_{1/2}$ atomic wave function [1]. The degeneracies are 4 and 2, respectively. Gallium phosphide does not only contain electrons, we must also consider phonons, which are quantized lattice vibrations [10]. Since phonons play a large role in the emission spectra of GaP, their dispersion relation in GaP is shown in Fig. 8 [11]. There are

four types of branches, longitudinal optical (LO), transverse optical (TO), longitudinal acoustic (LA), and transverse acoustic (TA). The long wave-length optical modes have opposite motion of the Ga- and P-sublattices, while the acoustic modes involve parallel motion of the atoms [10]. Due to the partly charged gallium and phosphorous atoms, the optical modes involve a dipole field, in contrast to the acoustic modes. In addition, the LO branch has an electric field associated to it in binary semiconductors [10]. The coupling to charged particles, like electrons, is thus expected to be large for LO phonons.

GALLIUM ARSENIDE PHOSPHIDE

Our understanding of alloys like $\text{GaAs}_{1-x}\text{P}_x$ is less complete than for non-alloy semiconductors, but it is steadily improving [12]. The use of luminescence for the study of semiconductor alloys seems to be a fruitful method [13]. The electronic structure is often treated by use of the virtual crystal approximation [14]. The random nature of the crystal is regarded to be a minor perturbation to an average " $\text{As}_{1-x}\text{P}_x$ " crystal and the concept of a $\mathbf{k}$ -vector is still useful. Anderson has pointed out the possible existence of two types of electron wave-functions in a random potential [15]. There may exist states corresponding to localized and non-diffusing particles in addition to the usual states delocalized over the whole crystal. Mott argues for the existence of mobility edges separating the energy eigenvalues of diffusing and non-diffusing states [12]. In the case of $\text{GaAs}_{1-x}\text{P}_x$, studied in this thesis, experiments show effects due to both band-structure and localization. Absorption measurements show the existence of narrow free excitons indicating a band-gap [16]. Luminescence studies, on the other hand, show both free excitons and other emission peaks, interpreted as being due to localized charge carriers [17,VI,VII]. Furthermore, the emission spectrum of the localized carriers shows a coupling to phonons which resembles the case of luminescence in a non-alloy semiconductor. The phonon coupling seen in luminescence will be dealt with later.

ELECTRONIC STRUCTURE OF EXCITONS BOUND TO NEUTRAL CENTRES IN GALLIUM PHOSPHIDE

The impurities treated here will be neutral and spin free in their ground state (with no exciton bound). This class of impurities are also called iso-electronic. For weakly bound excitons (in comparison with the band-gap), the electron and hole wave-functions are formed by linear combinations of conduction- and valence-band wave-functions. It is often reasonable to assume that the important contributions to the bound exciton wave-function originate from the extrema of these bands. Fig. 7 shows the effect of a point impurity on the states of the band extrema. If a point impurity is on a Ga-site, the three equivalent conduction band minima, transforming as X_3 , form a T_2 state. If the impurity is on a P-site they transform as X_1 and split into an A_1 state and an E state [1,9]. The part of the Hamiltonian causing this split is called the valley-orbit (V-O) interaction. If spin is present, a T_2 state is further split into a Γ_7 and a Γ_8 state by the spin-orbit interaction. An E or an A_1 state becomes a Γ_7 or a Γ_6 state, respectively. The lowest energy electron state is usually a Γ_7 or a Γ_6 state, while the lowest energy hole state is a Γ_8 state. The irreducible representations of the bound exciton will belong to the product representation of the electron and hole representations. The bound excitons studied in this thesis usually have one pair of singlet-triplet states [I,III], although sometimes two such pairs are seen [II]. The g-factor of the triplet state is in general isotropic. By ODMR measurements, the bound excitons studied here are seen to have a low or axial symmetry and are concluded to be defects composed of more than one atom.

Stress has a large influence on bound excitons [1,18]. The effect of stress on the conduction band minima is simpler than the effect on the top of the valence band. If uniaxial stress is along the $\langle 111 \rangle$ direction, the three conduction band valleys are equally affected. If the stress direction is away from the $\langle 111 \rangle$ direction, the valleys are affected unequally. This may lift an orbital degeneracy and cause more than one set of singlet-triplet pairs [19,II]. A strong enough central cell potential is also expected to lift the degeneracy due to the equivalent conduction band minima

(Fig. 7). Stress does not affect the electron g-factor, since the orbital contribution to the g-factor is close to zero [20]. The effect of a tensional or a compressional stress field on the $P_{3/2}$ hole states is shown in Fig. 8. If the stress is small, the effect of spin-orbit interaction dominates and is treated first. The spin-orbit interaction will split the T_2 state into a Γ_8 and a Γ_7 state. The fourfold degenerate Γ_8 state is lowest in hole energy and has $j=3/2$. After imposing a weak compressive axial stress field Γ_8 is split into Γ_6 and Γ_4, Γ_5 (degenerate by time-reversal). The Γ_6 state, lowest in hole energy, has $j=3/2$, but m_j is restricted to be $\pm 1/2$. If the stress is tensional, the ordering of the states is different with the Γ_4, Γ_5 states being lowest in hole energy [21]. A tensional stress field is often observed in GaP for complex defect such as Li-Li-O, Zn-O and Cd-O [3, 22, 23]. Luminescence measurements on the Li-Li-O bound exciton in a magnetic field reveal a splitting of the bound exciton levels consistent with a tensional stress field [3]. The orbital contribution to the hole g-factor causes a strong asymmetry of the g-factor (tensor) [3].

If the axial stress field is stronger than the spin-orbit interaction and is compressive, a different situation occurs, also illustrated in Fig. 8. The T_2 state in T_d symmetry is split into an A_1 and an E state in C_{3v} . The Γ_1 state has a quenched angular momentum and no magnetic effects arising from the orbital part of the wave-function [1]. The magnetic behaviour of the hole is caused by the spin part of the hole and shows no resolvable anisotropy in Zeeman measurements [I-III]. Including spin, the A_1 state becomes a Γ_6 state in C_{3v} , having $m_j=1/2$. The singlet-triplet pairs of many of the bound excitons studied here [I-III], have a g-factor that, from Zeeman data, is independent of the direction of the magnetic field, while in ODMR a residual anisotropy due to an axial symmetry is usually resolved [I-V]. They are concluded to experience a strong compressive axial stress field, essentially quenching the orbital part of the hole g-factor.

VIBRONIC STRUCTURE OF BOUND EXCITONS

As can be seen in Fig. 1, the emission from a bound exciton contains two parts - sharp lines originating from the exciton electronic energy levels, and a broad low-energy sideband. The sideband is formed when the exciton decays and simultaneously emits both a photon and one or more phonons (Figs. 1, 10).

The Hamiltonian for a crystal can be written:

$$H(\underline{r}, \underline{Q}) = H_e(\underline{r}) + H_L(\underline{Q}) + H_{eL}(\underline{r}, \underline{Q}) \quad (1)$$

where $\underline{r}$ and $\underline{Q}$ are the coordinates for all the electrons and all the nuclei, respectively [10]. $H_e(\underline{r})$ is the term acting only on the electron coordinates and $H_L(\underline{Q})$ is the term which only operates on the nuclear coordinates. $H_{eL}(\underline{r}, \underline{Q})$ finally couples the electron and nuclear motion. The eigenfunctions of eq. 1 can be written,

$$\Psi(\underline{r}, \underline{Q}) = \sum_j \phi_j(\underline{Q}) \psi_{ej}(\underline{r}, \underline{Q}_0), \quad (2)$$

$\phi_j(\underline{Q})$ describes the nuclear motion while $\psi_{ej}(\underline{r}, \underline{Q}_0)$ describes the electron motion [10, 24, 25, 26]. $\underline{Q}_0$, the fixed nuclear positions, can be chosen differently, but it is convenient to take $\underline{Q}_0$ to be the average position of the nuclei in some electronic state of the crystal such as the crystal ground state. Retaining one term in eq. 2 gives the adiabatic approximation [24, 25, 26].

The Schrödinger equation is:

$$H\Psi = \epsilon\Psi. \quad (3)$$

A solution for a set of levels in the band gap, in lowest order perturbation theory, is given by [26]

$$[H_e(\underline{r}) + H_{eL}(\underline{r}, \underline{Q}_0)] \psi_{ej}(\underline{r}, \underline{Q}_0) = \epsilon_{ej}(\underline{Q}_0) \psi_{ej}(\underline{r}, \underline{Q}_0) \quad (4a)$$

$$\sum_j [(H_L(\underline{Q}) + \epsilon_{ej}(\underline{Q}_0) - \epsilon) \delta_{kj} + V_{kj}(\underline{Q})] \phi_j(\underline{Q}) = 0 \quad (4b)$$

$$\Psi(\underline{r}, \underline{Q}) = \sum_j \phi_j(\underline{Q}) \psi_{ej}(\underline{r}, \underline{Q}_0), \quad (4c)$$

Here $V_{kj}(\underline{Q}) = \langle \psi_{ek} | H_1 | \psi_{ej} \rangle$, where $H_1 = H_1(\underline{r}, \underline{Q}) = H_{eL}(\underline{r}, \underline{Q}) - H_{eL}(\underline{r}, \underline{Q}_0)$. δ_{kj} is the Kronecker delta, which is zero unless $k=j$ when it is one. ϵ_{ej} is the electronic energy eigenvalue for the state ψ_{ej} evaluated at a fixed set of nuclear coordinates $\underline{Q}_0$, and ϵ is the total energy. If one state, $\psi_{ek}(\underline{r}, \underline{Q}_0)$, is non-degenerate and if $V_{kj}(\underline{Q}) = V_{kj}(\underline{Q}) \delta_{kj}$, eq. 4b simplifies to

$$[H_L(\underline{Q}) + \epsilon_{ek}(\underline{Q}_0) + V_{kk}(\underline{Q})] \phi_k(\underline{Q}) = \epsilon \phi_k(\underline{Q}), \quad (5)$$

which leads to one of the usual adiabatic approximations,

$$\Psi(\underline{r}, \underline{Q}) = \phi_k(\underline{Q}) \psi_{ek}(\underline{r}, \underline{Q}_0). \quad (6)$$

Various adiabatic approximations have been discussed by Markham [27]. Instead of using the expansion (2) one can expand,

$$\Psi(\underline{r}, \underline{Q}) = \sum_j \phi_j(\underline{Q}) \psi_{ej}(\underline{r}, \underline{Q}), \quad (7)$$

which converges more rapidly. $\psi_{ej}(\underline{r}, \underline{Q})$ is here a function of $\underline{Q}$ instead of being evaluated at a fixed $\underline{Q}_0$. The equation set 4a, 4b, 4c is more suitable for treating the problem of degenerate electronic levels interacting with vibrations [26], the Jahn-Teller problem [28, 29]. It is also convenient to use if the electronic levels of the system, e.g. an exciton, are closely spaced in comparison with typical phonon energies. Many bound excitons studied in this thesis have a singlet-triplet splitting of about 1 meV and the mixing of electronic states by electron-nuclear coupling might influence the phonon-assisted transitions [I-III]. The term $V_{kj}(\underline{Q})$ is a function of electronic wave-functions ψ_{ek} , ψ_{ej} . A further common simplification, is the harmonic approximation [10]

$$\phi_j(\underline{Q}) = \prod_m \phi'_m(\underline{Q}_m). \quad (8)$$

The total nuclear wave-function, $\phi_j(\underline{Q})$, is taken to be a product of independent harmonic wavefunctions, $\phi'_{jk}(\underline{Q}_k)$, one for each normal coordinate [10].

The term in eq. 4b

$$V_{kj}(\underline{Q}) = \langle \psi_{ek} | H_1 | \psi_{ej} \rangle, \quad (9)$$

is responsible for the phonon structure seen in emission. If $V_{kj}(\underline{Q})$ is expanded in a Taylor series,

$$V_{kj}(\underline{Q}) = V_{kj}^0 + \frac{\partial V_{kj}}{\partial \underline{Q}} \underline{Q} + \dots, \quad (10)$$

and the first two terms are kept, the result is the linear coupling approximation [30]. The matrix element associated with the second term is, by use of the Hellman-Feynman theorem [31]

$$\frac{\partial V_{kj}}{\partial \underline{Q}} \underline{Q} = \langle \psi_{ek}(\underline{Q}) | \frac{\partial H_1(\underline{Q})}{\partial \underline{Q}} | \psi_{ej}(\underline{Q}) \rangle = \underline{Q} \langle \psi_{ek} | \frac{\partial H_1}{\partial \underline{Q}} | \psi_{ej} \rangle. \quad (11)$$

H_1 has the symmetry of the impurity, A_1 , and consequently both $\underline{Q}$ and $\partial H_1 / \partial \underline{Q}$ belong to the same representation, though not necessarily A_1 [5]. $\underline{Q}$ has the same symmetry as the phonon and some phonons cannot couple linearly if $\langle \psi_{ek} | \partial H_1 / \partial \underline{Q} | \psi_{ej} \rangle = 0$. The phonon representations for a pure crystal have to be reduced to the proper point group in order to test the absence of phonon coupling given the above approximations. The reductions for common symmetry points are tabulated in Table 1, for the zinc-blende and diamond lattices, under the T_d point group. Above, the average position of the nuclei has been assumed to be the crystal ground state, but it is usually different in the excited state, illustrated in Fig. 9. This difference in average position changes, with the emission of one or more phonons, when an electronic transition occurs.

The strength of the phonon coupling is different for different type of phonons. LO phonons with an associated electric field, (in semiconductors with two different atoms in the basis), interact strongly with charge carriers, the so called Fröhlich interaction [32, 33]. The situation is less clear for the exciton-LO phonon interaction, since the exciton is neutral but polarizable [1, 32]. The acoustic phonons, TA and LA, do not necessarily carry an electric

field, nor a dipole field [10]. The in-phase motion of the atoms in this case cause a local change in the bandgap, through the strain field associated with the atomic motion. This strain field couples to the exciton, and the coupling is called deformation potential coupling [33,34]. The deformation potential coupling is also present for the optical phonons. In addition, there might be a piezo-electric coupling, if the crystal is piezo-electric [33,34]. The atomic motion then produces an electric field even for acoustic phonons.

A bound exciton being localized in space has a distribution of $\mathbf{k}$ -vectors over the Brillouin zone, and can therefore interact with phonons with large and small $\mathbf{k}$ -vectors. The electron and hole phonon interaction is dependent on the difference in charge distribution between the initial, $\rho_i(\underline{r})$, and final states, $\rho_f(\underline{r})$, through the following relation [33,34],

$$H_{eL} = \int (\rho_i(\underline{r}) - \rho_f(\underline{r})) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (12)$$

For the excitons studied in this thesis it is perhaps expected that the extent of the wave-function is comparable for the different states present in the exciton ground state, since the energy difference between these states is small (≈ 1 meV), compared with the binding energy (≈ 100 meV) [I-III].

LUMINESCENCE FROM GALLIUM ARSENIDE PHOSPHIDE

The band structure of $\text{GaAs}_{1-x}\text{P}_x$ changes from indirect when $x < 0.46$ to direct when $x > 0.46$ [35,36]. The luminescence is broad due to fluctuations in the alloy composition and is due mainly to donor-bound excitons, free excitons and donor-acceptor or conduction-band to acceptor emissions [16]. Nitrogen impurities have been extensively studied [16,36,37].

Emissions due to excitons localized by alloy fluctuations [40], are sometimes seen in alloys, such as $\text{CdS}_{1-x}\text{Se}_x$ [2,38]. Although thought to be localized in space, diffusion within the emission line, spectral diffusion, seems to take place [2,38]. This also occurs for the nitrogen bound exciton [37]. The emission due to localized charge

carriers, M_0^x , seen in indirect gap ($x > 0.46$) $\text{GaAs}_{1-x}\text{P}_x$ has a sharp high-energy edge [VI,VII]. Such a sharp feature in the emission from an alloy raises suspicion and the explanation has to be sought in the statistics of a large number of random potentials. Mechanisms for a sharp feature can be found in the picture of mobility edges [12], and in percolation theory. A mobility edge is a well-defined energy, separating localized and non-localized states in a random potential. The effect of Coulomb repulsion between electrons in disordered solids and its effect on localization is not well understood [12]. The high energy edge of M_0^x may correspond to a mobility edge.

A more deeply bound state is usually thought to be more localized than a shallow state [12]. The M_0^x high-energy edge may alternatively correspond to a critical extension of the wave-function. If the wave-function is larger than this critical extension, the state decays non-radiatively. It is argued in papers VI and VII that the M_0^x emission is due to the recombination of separated, individually localized, electrons and holes.

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- [1] P.J. Dean and D.C. Herbert in *Topics in Current Physics*, Vol. 14, Excitons, ed. K. Cho, (Springer Verlag, 1979), pp.55-182.
- [2] S. Permogorov, A. Reznitskii, S. Verbin, G.O. Muller, P. Flögel, and M. Nikiforova, *Phys. stat. sol. (b)* 113, 589 (1982).
- [3] P.J. Dean, *Phys. Rev. B* 4, 2596 (1971).
- [4] B.C. Cavenett, *Advances in Physics*, 30, 475 (1981).
- [5] M. Tinkham, *Group Theory and Quantum Mechanics*, (McGraw-Hill, New York 1964).
- [6] G. Dresselhaus, *Phys. Rev.* 100, (1955).
- [7] B. Monemar and L. Samuelson, *Sol. St. Comm.* 26, 165 (1978).
- [8] M.L. Cohen and T.K. Bergstresser, *Phys. Rev.* 141, 789, (1966).
- [9] T.N. Morgan, *Phys. Rev. Lett.* 21, 819, (1968).
- [10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, (Oxford University Press, Oxford, 1962).
- [11] J.L. Yarnell, J.L. Warren, R.G. Wenzel and P.J. Dean, *Neutron Inelastic Scattering*, 1, 301, (Vienna, 1968).
- [12] N.F. Mott and E.A. Davies, *Electronic Processes in Non-Crystalline Materials*, (Oxford University Press, Oxford, 2. ed. 1979).
- [13] R.J. Nelson, N. Holonyak Jr. and W.O. Groves, *Phys. Rev.* B13, 5145, (1976).
- [14] H. Ehrenreich and L.M. Schwartz, *Sol. St. Phys* 31, 149 (1976).
- [15] P.W. Andersson, *Phys. Rev.* 109, 1492 (1958).
- [16] R.J. Nelson in *Excitons*, edited by E.I. Rashba and M.D. Sturge (North-Holland, 1982).
- [17] S. Lai and M.V. Klein, *Phys. Rev. Lett.* 44, 1027 (1980).
- [18] G. Davies, *J. Phys.* C17, 6331 (1984).
- [19] H.P. Gislason, B. Monemar, P.J. Dean and D.C. Herbert, *Physica* 117B & 118B, 269, (1983).
- [20] P.J. Dean, R.A. Faulkner and S. Kimura, *Phys. Rev.* B2, 4062 (1970).
- [21] J. v. W. Morgan and T.N. Morgan, *Phys. Rev.* B1, 739, (1970).
- [22] C.H. Henry, P.J. Dean and J.D. Cuthbert, *Phys. Rev.* 166, 737, (1968).
- [23] T.N. Morgan, B. Welber and R.N. Bhargava, *Phys. Rev.* 166, 751, (1968).
- [24] M. Born and J.R. Oppenheimer, *Ann. Physik* 84, 457 (1927).
- [25] A.M. Stoneham, *Theory of Defects in Solids*, (Oxford, 1975).

- [26] H.J. Zeiger and G.W. Pratt, *Magnetic Interactions in Solids*, (Clarendon Press, Oxford, 1973).
- [27] J.J. Markham, *Phys. Rev.* **103**, 588 (1956).
- [28] J.H. van Vleck, *J. Chem. Phys.* **7**, 72 (1939).
- [29] M.D. Sturge, *Sol. St. Phys.* **20**, 92 (1967).
- [30] K.K. Rebane, *Impurity Spectra of Solids*, (Plenum Press, New York, 1970).
- [31] R. Feynman, *Phys. Rev.* **56**, 340 (1939).
- [32] P.Y. Yu in *Topics in Current Physics*, Vol. 14, Excitons, ed. K. Cho, (Springer Verlag, 1979).
- [33] C.B. Duke and G.D. Mahan, *Phys. Rev.* **139**, A1965 (1965).
- [34] A.M. Stoneham, *J. Phys.* **C12**, 891 (1979).
- [35] D.J. Wolford, J.A. Bradley, K. Fry, J. Thompson and H.E. King, *Proc. 13th Int. Symp. on Gases and related Compound*, Alberquerque, Sept. (1982).
- [36] J.A. Kash, J.H. Collet, D.J. Wolford and J. Thompson, *Phys. Rev.* **B27**, 2294 (1983).
- [37] H. Mariette, V. Thierry-Mieg, J. Chevallier and P. Leroux Houghon, *Physica* **117B&118B**, 102 (1983).
- [38] E. Cohen and M.D. Sturge, *Phys. Rev.* **B25**, 2528 (1982).
- [39] F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transitions in Solids*, (Pergamon Press, Oxford, 1975).
- [40] L. Samuelson, *Proc. 13th Int. Conf. on Defects in Semicond.*, Coronado 1984, (to be published in *J. Electr. Mat.*).

DIAMOND		ZINCBLLENDE	DIAMOND	ZINCBLLENDE
Γ_1	A_1	A_1	X_1	$A_1 + E$
Γ_2	A_2	A_2	X_2	$A_2 + E$
Γ_3	E	E	X_3	T_2
Γ_4	T_1	T_1	X_4	T_1
Γ_5	T_2	T_2	X_5	$T_1 + T_2$

DIAMOND		ZINCBLLENDE	DIAMOND	ZINCBLLENDE
L_1	$A_1 + T_2$	$A_1 + T_2$	Δ_1	$A_1 + E + T_2$
L_2	$A_2 + T_1$	$A_2 + T_1$	Δ_1'	$A_2 + E + T_1$
L_3	$E + T_1 + T_2$	$E + T_1 + T_2$	Δ_2	$A_2 + E + T_1$
L_1'	$A_1 + T_2$	$A_1 + T_2$	Δ_2'	$A_1 + E + T_2$
L_2'	$A_2 + T_1$	$A_2 + T_1$	Δ_3	$2T_1 + 2T_2$
L_3'	$E + T_1 + T_2$	$E + T_1 + T_2$	Δ_4	

Table over representations of sets of wave-functions, at different symmetry points in diamond and zincblende lattices, reduced under T_d . The representation-labels for the L and Δ points in diamond symmetry are taken from ref. 39. The Δ_3 and Δ_4 representations of the little group of k in zincblende are degenerate by time reversal.

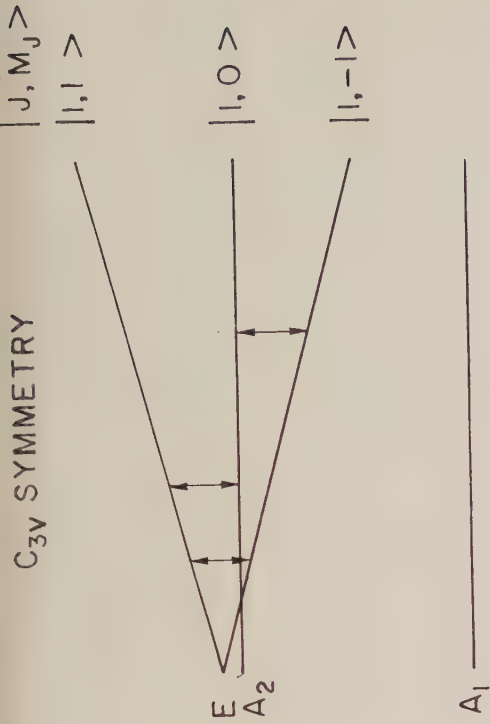


Fig. 2 A schematic illustration of ODMR on a triplet system, in this case a triplet excitation in trigonal symmetry. The E and A₂ levels decay to an A₁ state giving luminescence. The transition rate from the A₂ state is usually lower than from the E states. If the A₂ state is saturated, but the E states are not, the micro-wave transitions between the E and A₂ states will increase the total luminescence from the three levels (E, A₂).

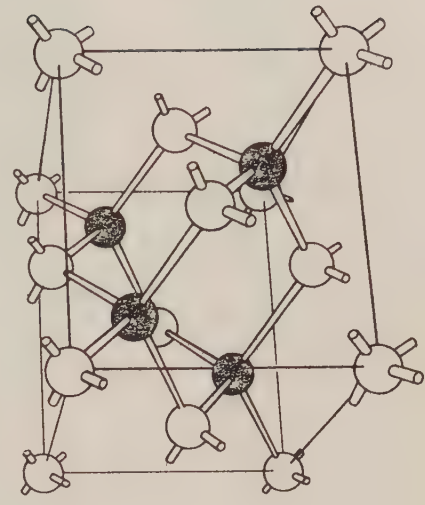


Fig. 3 The zincblende lattice. It is formed by two interlocking fcc-lattices offset by one quarter of the cube diagonal.

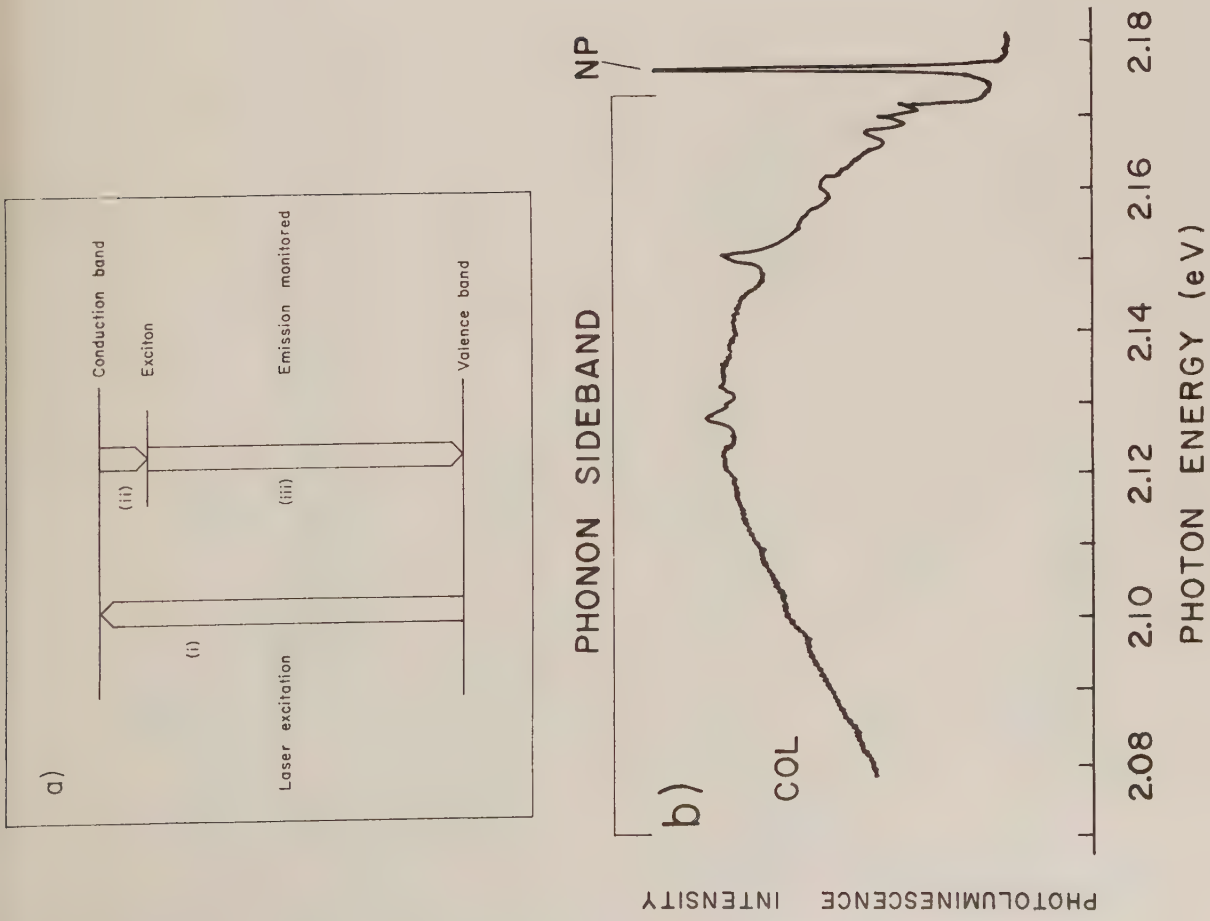


Fig. 1 (a) An illustration of photoluminescence showing laser excitation (i), followed by exciton formation (ii). The final decay of the exciton (iii), is then measured. (b) A spectrum of a typical exciton emission, showing the phonon lines and the phonon sideband.

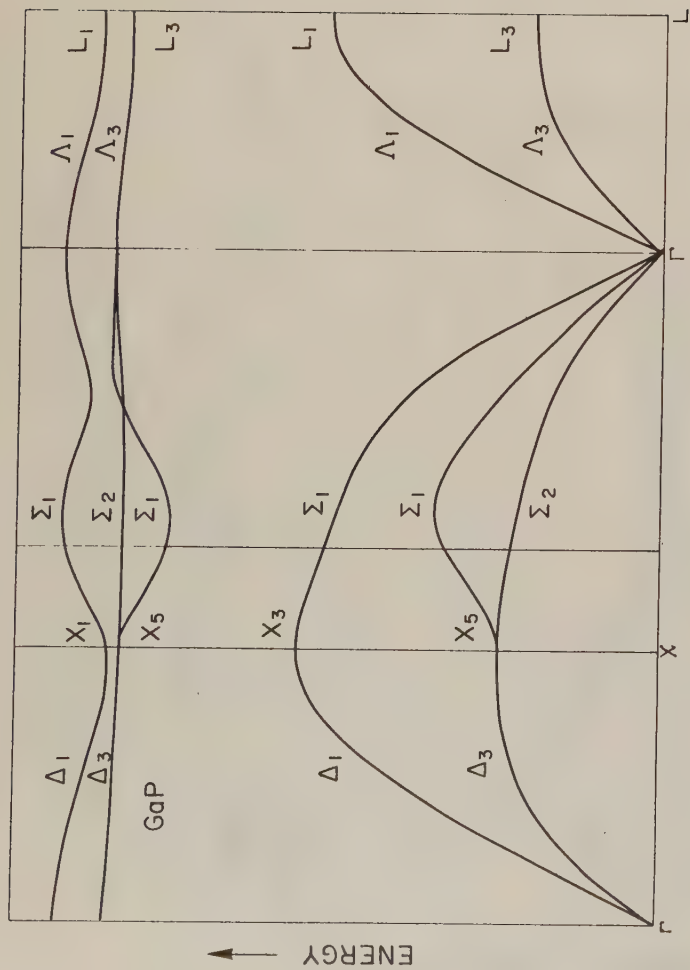


Fig. 4 The band-structure of Gallium Phosphide, showing various symmetry points. The origin of the T_d point group is on a phosphorous site.

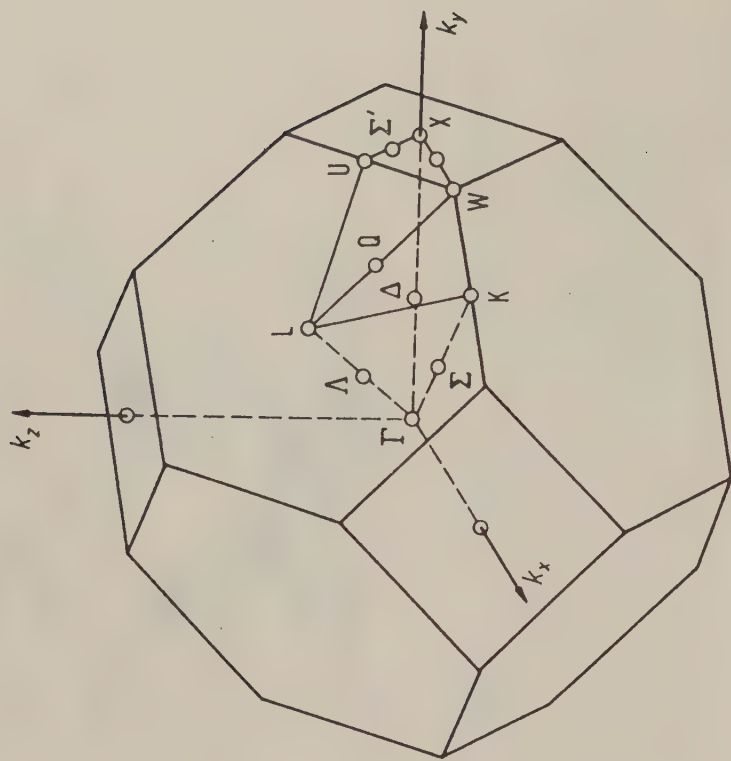


Fig. 5 Brillouin zone for the zincblende lattice. The valence band top is at the Γ -point and the conduction band minima are at the X -points.

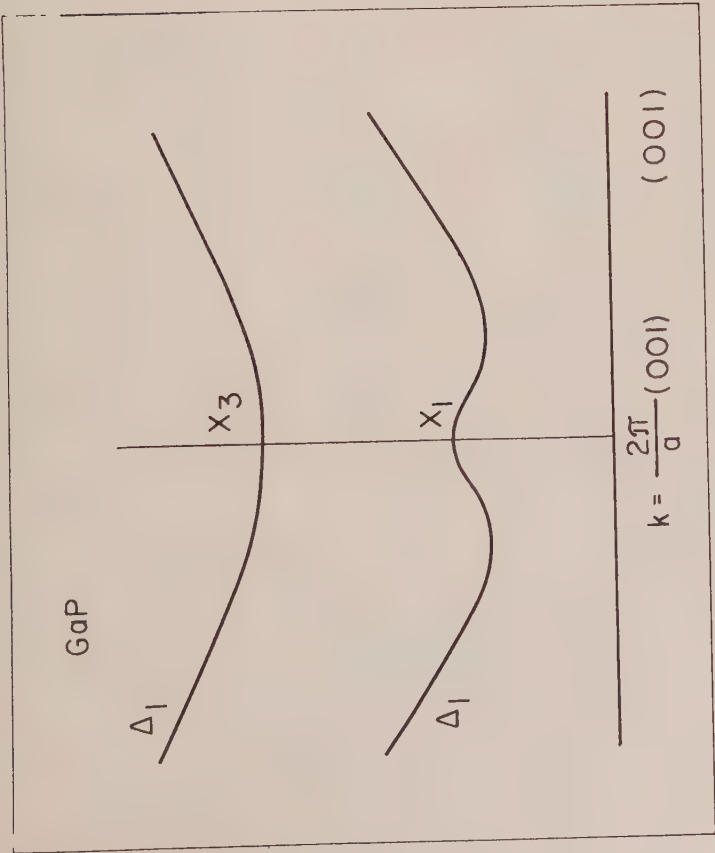


Fig. 6 A close view of the band-structure around the X-point. The conduction band minima are not exactly at the X-point, a feature known as camel's back.

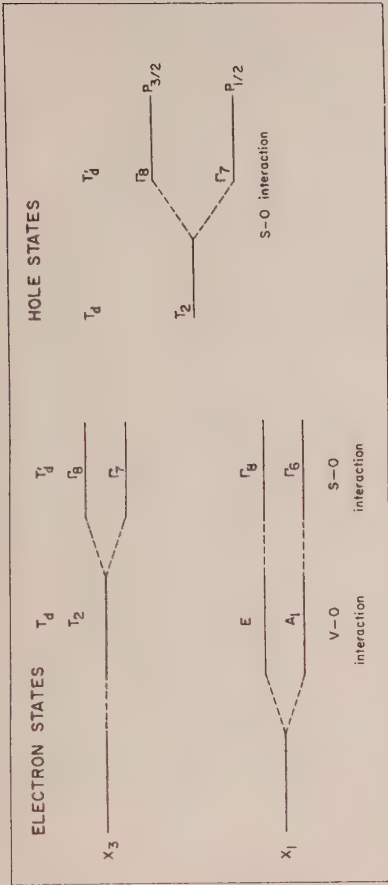


Fig. 7 (a) The representations for electron states under the T_d and T_d' point groups. X_1 and X_3 are the representations under the little group of $\underline{k}$.

(b) Neglecting spin, a hole from the top of the valence band transforms as T_2 under T_d . When spin is introduced a splitting into a Γ_8 and a Γ_7 state occurs. These states transform as $P_{3/2}$ and $P_{1/2}$ atomic wave-functions respectively.

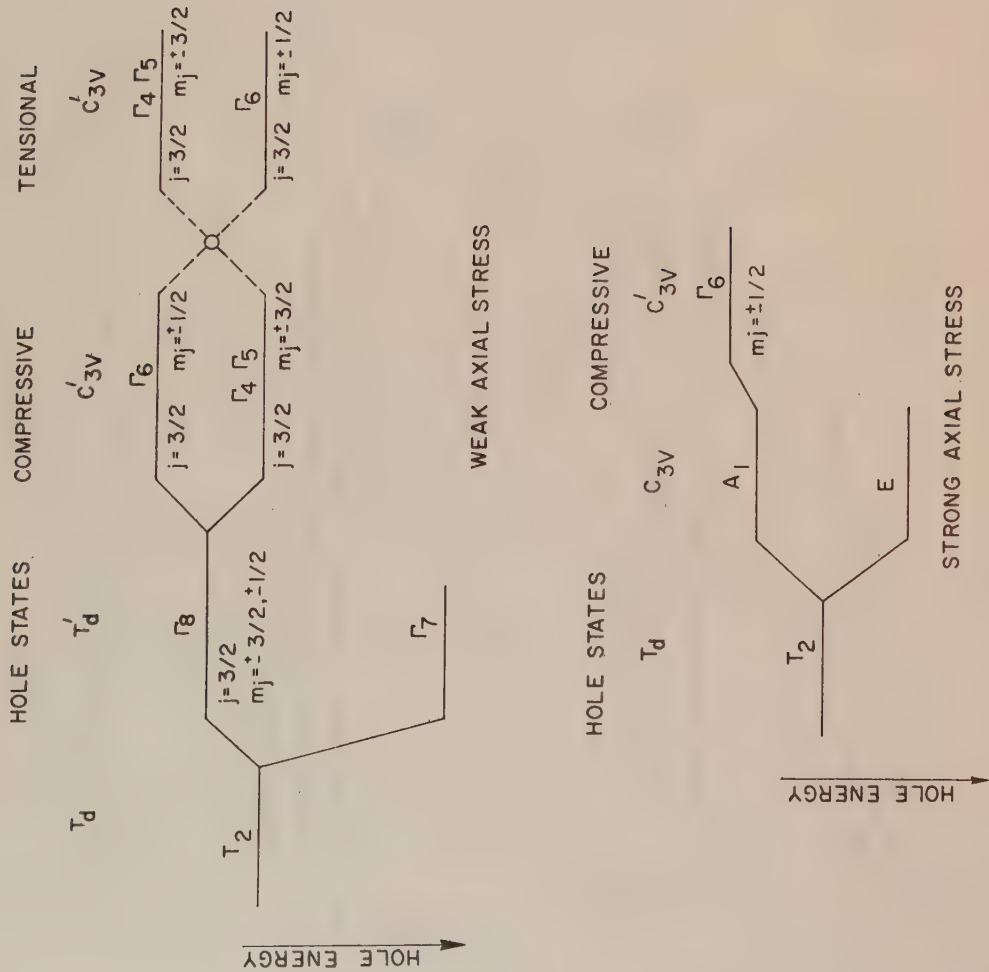


Fig. 8 The effect of weak and strong axial fields on the valence band hole states. For a weak axial stress, less than the spin-orbit interaction, the lowest energy hole state has $j=3/2$. This fourfold degenerate state will split into two states according to their m_j values, and the energy order is dependent on the sign of the stress, as indicated. If the stress is strong, the perturbation by the stress field has to be calculated first [1], and the resulting state has a quenched angular momentum, giving a pure spin state.

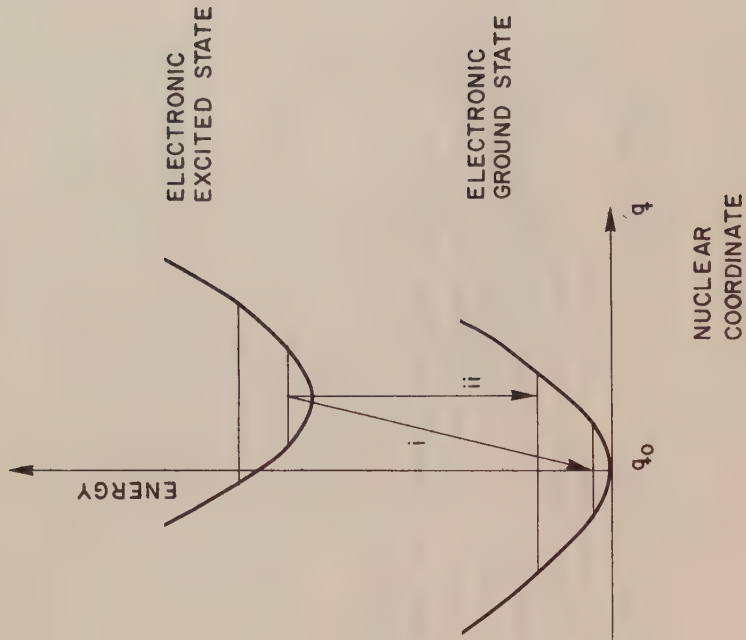


Fig. 9 An illustration of why phonon structure is seen in luminescence. In each electronic state there are many vibrational states. In case (i) the vibrational state is the vibrational ground state both in the initial and final states of the transition, giving a no-phonon line. In case (ii), the transition is to a vibrationally excited electronic ground state giving a phonon-assisted transition.

Neutral (Cu-Li) complexes in GaP: The $(\text{Cu-Li})_I$ bound exciton at 2.306 eV

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Several new emissions due to excitons bound at neutral complexes are observed in GaP upon diffusion with Cu and subsequently with Li. Here we report work on the most shallow of these centers, with lowest electronic transition at 2.306 eV. This center which we denote as $(\text{Cu-Li})_I$ is studied by means of photoluminescence, photoluminescence excitation and magnetooptical work. The luminescence spectrum exhibits a pair of electronic lines of singlet-triplet multiplicity as revealed by magnetic field measurements. This configuration has been shown to be characteristic for certain defect complexes in cubic semiconductors. These centers are dominated by a strong axial strain field combined with a hole attractive central cell of the neutral complex. Optically detected magnetic resonance measurements determine the symmetry of the $(\text{Cu-Li})_I$ complex as orthorhombic with the z-axis $\langle 111 \rangle$ -oriented. The phonon sideband of the luminescence is richly structured and the well resolved phonon spectra contain two true local modes and a gap mode in addition to the usual zoneboundary modes of GaP. The local modes show substantial energy shift when replacing ^7Li with ^6Li thus proving the

+ Deceased

presence of Li in the complex. No new local modes appear after mixed isotope doping indicating the presence of only one Li-atom. Lifetime measurements reveal a very long decay time for the triplet line of $\tau = 1$ ms, whereas the singlet has a more allowed character with $\tau = 20$ μs . The long radiative lifetime is consistent with no free spin in the final state of the transition. This agrees with the observed thermalisation between the magnetic subcomponents of the triplet, proving that the splitting in magnetic field occurs in the initial state of the transition. The compiled data suggest an orthorhombic $\langle 111 \rangle$ -oriented complex consisting of Cu_{Ga} in combination with a pair of interstitial atoms, of which one is known to be Li, as the identity of the $(\text{Cu-Li})_I$ center.

I. Introduction

Properties of defects in semiconductors and their identification are problems of great current interest. Such defects are characterized and well understood only in some simple cases such as substitutional point defects. Even in this case problems still exist in identifying the so called deep level substitutional defects (1). Unfortunately, high temperature chemical reactions during growth or heat treatment and the subsequent cool down seem to favour the creation of various complexes of impurity atoms and other point defects, in particular for compound semiconductors (2). The electronic properties of such complexes are even more difficult to predict. Yet, these defects may be very important as persistent recombination centers in semiconductors, for the reason that they often can capture and bind both kinds of carriers (3). In addition, they may transform into electrically active centers via defect reactions during various processing steps, such as device fabrication.

Some of the most successful cases of characterization of defect complexes in semiconductors have been carried out with optical spectroscopy, notably for those centers where bound excitons (BE) can be observed (3). For the reason of charge neutrality and Coulomb attraction during defect formation at high temperature the most abundant type of complexes are believed to be the electrically neutral associates, often referred to as molecular isoelectronic defects (3). The atoms forming such complexes are arranged to compensate for all valence electrons of the host lattice sites they occupy, so as to give neutral substitutes. Both an electron and a hole (a bound exciton) may be bound to each of these centers at low temperature. This type of defect has been studied in some detail in materials such as GaP. Good examples are the Zn-O and Cd-O complexes occupying nearest neighbour sites (4,5), and the so called NN-pairs consisting of two N atoms substituted at P-sites separated by various distances (6). Electronically these particular cases are reasonably well understood in terms of the so called Hopfield-Thomas-Lynch model (7). Here one particle is deeply bound in a localized potential (the electron in the above mentioned examples) while the second particle is bound in a shallow state by the Coulomb-like potential of the primary particle (7). The electronic properties of the bound exciton thereby formed can usually be understood in terms of the expected electron hole (J-J) splitting and internal axial strain field of the defect (3,8).

A more complicated class of complexes arises when interstitial atoms also are involved. A good example of such a case is the linear $\text{Li}_i\text{-Li}_{\text{Ga}}$ - O_p <111>-oriented defect in GaP, which has been studied via its bound exciton spectra (9). In this case all observed electronic states of the excitons are within a few meV of the lowest state (at 2.087 eV at 2 K).

The splittings are again explained in a satisfactory way by a moderate J-J splitting and a weak axial strain field (9). A recent study of the COL defect in GaP with the lowest BE state at 2.1774 eV (concluded to be a $\text{Cu}_i\text{-Cu}_{\text{Ga}}$ -complex), on the other hand, reveals a case with a much stronger effect of the axial field and also a very strong J-J splitting (10). Similar, but even stronger effects of axial field and exchange interaction are observed for the bound exciton at 1.911 eV in GaP, ascribed to a <100>-oriented complex (11). Both these luminescence bands have been found to disappear upon Li-diffusion for diffusion temperatures larger than 350 °C, while new emissions are introduced (12,13).

As a continuation of these studies we report here the results of an investigation with optical spectroscopy on neutral complexes of isoelectronic character formed by the interaction of Cu and Li in GaP. Both these group I species are fast interstitial diffusers, and as an isolated impurity Li has so far only been found to occupy interstitial sites while the case of Cu is more uncertain. In complexes both should be able to occupy Ga-sites (9,10). Doping with Li and Cu is therefore expected to create neutral associates involving both Ga-sites and interstitial sites. Several different complexes may be expected, depending on which of the atoms (Cu or Li) occupies a Ga-site, the number of each species involved, and which interstitial sites they occupy. We have observed at least five different Cu-Li spectra appearing in GaP after a subsequent Li-diffusion into Cu-doped material. These centers labelled $(\text{Cu-Li})_{\text{I-Y}}$ are characterized by their different BE luminescence spectra, all of them being neutral molecular associates. The subject of this paper, $(\text{Cu-Li})_{\text{I}}$, is the most shallow center, binding an exciton with lowest electronic transition at 2.306 eV. The $(\text{Cu-Li})_{\text{II}}$ center binds an exciton at 2.276 eV, $(\text{Cu-Li})_{\text{III}}$ at 2.242 eV (12), $(\text{Cu-Li})_{\text{IV}}$ at 2.116 eV, and the $(\text{Cu-Li})_{\text{Y}}$ center has the

lowest BE line at 2.172 eV (13). Besides the $(\text{Cu-Li})_{\text{I}}$ center, $(\text{Cu-Li})_{\text{III}}$ and $(\text{Cu-Li})_{\text{V}}$ show particularly strong and persistent PL bands and are the subject of separate publications (12,13). The $(\text{Cu-Li})_{\text{III}}$ center has been shown to have a trigonal $\langle 111 \rangle$ oriented symmetry from optically detected magnetic resonance (ODMR) data. A model for its identity as a linear $\text{Li}_1\text{-Cu}_{\text{Ga}}\text{-Cu}_i$ neutral associate was proposed (12).

In this study we present photoluminescence (PL) spectra for the $(\text{Cu-Li})_{\text{I}}$ center. Also, the splitting of the electronic lines in a magnetic field is reported. To achieve information on all electronic states, photoluminescence excitation (PLE) spectra were recorded with a cw dye laser excitation. It appears that the observed electronic states are fairly close together for this center (J-J splitting only 1.0 meV). This indicates a moderate exchange interaction for the bound exciton. The BE spectra are consistent with an exciton binding at a center with reduced local symmetry rather than at a point defect site. The local strain field is deduced to have a compressional sign, and its symmetry is determined as orthorhombic from ODMR measurements.

In Sec. II below, the procedure of crystal preparation and doping is described. The experimental techniques for measuring optical spectra are also outlined. Sec. III A contains detailed photoluminescence data at low temperatures. PL spectra taken at various temperatures slightly above 2 K reveal differences in phonon coupling for the two electronic states. Sec. III A also includes Zeeman data for the electronic lines which shows that the $(\text{Cu-Li})_{\text{I}}$ center exhibits a magnetic triplet-singlet structure, often observed as a consequence of a compressional axial field interacting with BE states. In Sec. III B excitation spectra for the center are shown, giving the relative oscillator strengths of the electronic states. In section III C a summary of the ODMR results for the $(\text{Cu-Li})_{\text{I}}$ center is presented. Sec. IV contains a more detailed

discussion on the possible identity of the $(\text{Cu-Li})_{\text{I}}$ complex, suggested from both electronic and vibrational properties, ODMR data and Li-isotope doping as well as comparison with other previously studied neutral complexes involving Cu and Li (12,13).

II EXPERIMENTAL

II A. Crystal preparation

The starting material used in these investigations was mostly n-type or p-type liquid-encapsulated-Czochralski (LEC) grown bulk material. Epitaxial wafers and solution grown material were also used. Luminescence studied on the solution grown starting material showed the presence of C, S, Si and N in various concentrations, usually low and often the corresponding BE lines were barely detectable. No correlation with the spectra described in this paper was found for any of these impurities. The impurity concentration was generally higher in the bulk material. In such crystals the $(\text{Cu-Li})_{\text{I}}$ luminescence was always weak or absent for all types of shallow doping. It was very strong in solution grown crystals however. This spectrum also appeared strongly in epitaxial wafers, although the $(\text{Cu-Li})_{\text{III}}$ luminescence (12) (with lowest electronic transition at 2.242 eV) is always of comparable strength in these samples. This is in contrast to the solution grown crystals where $(\text{Cu-Li})_{\text{I}}$ always dominates.

For the initial Cu-diffusion Cu was evaporated on the surface of the crystal to a thickness of 600-1400 Å. The crystals were then placed in a fused SiO_2 ampoule together with a protective GaP-Ga melt. The ampoules were evacuated and sometimes backfilled with dry N_2 gas. The crystals were diffused at temperatures between 900 and 1100 °C followed

by a rapid quenching in water to room temperature. Residual Cu was cleaned from the GaP surface with 40% HCl and the crystals were washed in distilled water. This diffusion procedure causes the COL center to appear strongly in luminescence (10), thus proving the presence of Cu in the samples. Samples were doped either with natural Cu or with the pure isotopes ^{63}Cu and ^{65}Cu .

In the Li-doping step the crystals were placed in a quartz ampoule together with a small pellet of metallic Li. For high diffusion temperatures the Li metal was often placed on a piece of quartz. This reduced the risk of Li reacting with the tube wall due to chemical reactions with SiO_2 .

Isotope doping was made by using separately natural Li metal representing the ^7Li isotope and enriched Li metal for the ^6Li isotope. The natural abundance of Li is 92.6% ^7Li and 7.4% ^6Li . The commercially available enriched metal used had 95.5% ^6Li and 4.5% ^7Li . We also performed a series of mixed isotope doping with approximately equal quantities of each isotope in the ampoule. We could not account for the possibility of different diffusion rates of the Li isotopes. Judging from the local mode spectra, however, we found that both isotopes were present in the defect. (See below under Section 3).

The Li-diffusion was performed at temperatures between 250 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$. The diffusion time varied from 20 minutes at 1000 $^{\circ}\text{C}$ to 4 hours at 250 $^{\circ}\text{C}$. After the diffusion the ampoules were quenched to room temperature in water or air with similar results. It was found that $T=450$ $^{\circ}\text{C}$ produced the best $(\text{Cu-Li})_I$ spectra, but the spectrum appears after diffusion at all temperatures between 250 $^{\circ}\text{C}$ and 850 $^{\circ}\text{C}$. For all diffusion temperatures above 350 $^{\circ}\text{C}$ the strong Cu-related COL emission (as well as other Cu-related emissions when present) always disappeared comple-

tely, while new Cu-Li spectra appeared strongly. Sometimes the well known $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_p$ spectrum (9) with electronic ground state at 2.087 eV also appeared indicating the presence of O in those samples. None of the spectra assigned to Cu and Li showed any shift with changes in O isotope, however. Thus the corresponding complexes are unlikely to involve O. Li doping alone produced only the shallow DA-pair spectra involving the two inequivalent Li_i donors and their corresponding BE spectra close to the bandgap (14). None of the new Cu-Li BE spectra and particularly not the $(\text{Cu-Li})_I$ spectrum described in this paper are found with Li-doping alone. This further proves their association with both Cu and Li.

II B. Optical measurements

Photoluminescence measurements were performed either with Ar^+ or Kr^+ cw laser excitation at temperatures varying from 1.8 K up to 30 K. PL spectra were obtained with a Jarrel Ash 0.75 m double grating monochromator and with a 2 m Bausch and Lomb single grating spectrograph. The signals were recorded with a Nicolet 1170 signal averager. Magneto-optical data were obtained with a Varian electromagnet at fields up to 3.5 T and a superconducting magnet at fields up to 6 T. Excitation spectra were performed with cw dye laser excitation, mostly with narrow band detection through the 0.75 m double monochromator to select out a suitable part of the spectrum. Sometimes broad band detection with a filter was employed. Lifetime measurements were performed at RSRE using cathodoluminescence at about 10 K and at Hull University employing conventional pulsed laser techniques.

III Experimental results

III A. Low Temperature Photoluminescence Spectra

A typical low temperature photoluminescence spectrum from Cu-Li codoped GaP is shown in Fig. 1. It is dominated by the $(\text{Cu-Li})_I$ spectrum involving sharp electronic lines with a phonon-assisted wing at lower energies. The shallow $(\text{Cu-Li})_I$ center occurs with two electronic lines L_I^1 and L_I^2 at 2.3072 eV and 2.3062 eV respectively. The sharpness and energy positions of the lines indicate that they are electronic transitions from a bound exciton complex (3). Investigation in a magnetic field of 3.5 T shows that the lower energy line L_I^2 is a magnetic triplet ($J=1$) with an isotropic g value. The higher energy component L_I^1 does not split in a magnetic field, see inset in Fig. 1. Thermalization between the magnetic subcomponents is observed in luminescence. Thus it is concluded that the splitting occurs in the initial state of the transition which is an evidence for the identification as a BE transition to a spin-free final state.

A rich phonon spectrum occurs with the $(\text{Cu-Li})_I$ exciton. The coupling strength is rather weak however. In contrast with many deeper centers the small exciton localization energy for the $(\text{Cu-Li})_I$ center results in a luminescence spectrum which clearly reveals the one-phonon density of states of the GaP host. This coupling is induced by delocalization of the electron wavefunction in k-space.

In Figs. 2a,b the phonon side band of the $(\text{Cu-Li})_I$ luminescence is shown in detail. Phonon energies and interpretations of the most prominent peaks are listed in Table I. Phonon coupling to the X-zone boundary phonons is present as expected for the case of a spin-forbidden triplet transition. At phonon energy of 13.1 meV we observe the

TA^X phonon replicas of both singlet and triplet BE components. The coupling is stronger to the triplet L_I^2 as a consequence of the selection rules. This can be clearly seen at elevated temperature, where the electronic singlet line dominates, but both TA^X replicas have comparable strength, in spite of the weak triplet line (Fig. 2b), illustrating the different phonon coupling to the components as commonly observed for such systems (3,12).

The LA^X components are partly overlapping with an independent electronic BE transition labelled $(\text{Cu-Li})_{II}$ in Fig. 1. It occurs at 2.2758 eV in epitaxial layers under the same doping conditions as the $(\text{Cu-Li})_I$ center. However, the LA^X component of the triplet line is clearly observed. In solution grown samples the $(\text{Cu-Li})_{II}$ center is weak or absent (Fig. 2). At lower energies TO^X components are found in the spectrum with phonon energy 45.2 meV. As before the triplet L_I^2 shows stronger coupling to this mode. On the other hand, both electronic components have similar coupling strength to LO^T , which is represented by a pronounced peak at a phonon energy of 50.2 meV. A weak coupling to TO^T is also present, 45.7 meV below the electronic lines. All these zone-boundary phonon energies agree well with earlier data from BE measurements in GaP (3,5).

Localized phonon modes can give important clues for the identification of defect complexes for which the exact chemical identities are not known. Such localized modes can be classified as true local modes of energy higher than the host lattice vibrations, gap modes with energy between the optical and acoustic bands, and inband resonance modes. A rather striking example of the last type of mode in the $(\text{Cu-Li})_I$ spectrum is the occurrence of a broad band of what seems to be sharp replicas peaking at about 2.296 eV. Since this band of quasilocalized modes with energies about 10-12 meV is strongest at temperatures where the singlet L_I^1 is dominating, this phonon coupling seems to be related to the singlet.

A prominent gap mode occurs at a phonon energy of 37.7 meV (Fig. 2) This phonon couples equally to both components of the electronic line. True local modes also appear in the $(\text{Cu-Li})_I$ spectrum, stronger than usually found in BE spectra. There are two local modes present, each coupling with similar strength to both electronic components. The weaker phonon mode has the energy 51.2 meV and the stronger one 52.8 meV (Fig. 2). These local peaks are relatively sharp and their intensities make it possible to perform isotope doping in order to reveal the nature of the corresponding vibrational modes. The result is shown in Fig. 3 and Table II.

Upon doping with ^6Li a marked shift occurs in both local mode energies. The 51.2 meV mode shifts to 52.4 meV, which is not to be confused with the 52.8 meV mode of ^7Li . The resolution in Fig. 3 clearly resolves the 0.4 meV energy difference. The 51.2 meV replica of the L_I^1 singlet is only detectable at higher temperatures when the L_I^2 triplet has vanished since it overlaps its L_O^1 replica.

The 52.8 meV mode shifts in energy to 55.6 meV with ^6Li doping. This shift is larger than for the lower energy local mode. When doping with natural Li a small peak is observed at 55.6 meV. The relative ratio of this peak to the strong 52.8 meV mode approximately agrees with the abundance of ^6Li in natural Li (7.4% ^6Li).

The mixed isotope doping did not reveal any new local modes in addition to the pure ones, as can be seen in Fig. 3. Judging from the relative strength of the ^7Li and ^6Li local modes, which are now observed in the same spectrum, we conclude that both isotopes are present in the complexes in approximately equal concentrations. Some variation is observed in different experiments, though. The good resolution in these experiments rules out the possibility that any replicas of the same or-

der of magnitude could remain unrevealed in the PL spectra. This result is important since the absence of new local modes for approximately equal amounts of both Li isotopes evidently means that there is only one Li atom vibrating in the $(\text{Cu-Li})_I$ complex in the simplest model. As discussed below in Sec. IV two or more Li atoms would give rise to mixed modes involving both isotopes simultaneously if they are not vibrationally isolated from each other.

A slight increase in temperature has a profound effect on the relative intensities of the two electronic lines in the $(\text{Cu-Li})_I$ spectrum. Thermal population causes the higher singlet state to become much stronger at elevated temperature at the same time as the triplet gradually disappears. Apparently the $J=0$ singlet has an appreciably higher oscillator strength than the lower energy triplet. This is also shown by the PLE measurements reported in the next section.

III:B Excitation Spectra

To gain information on the existence of further electronic excited states beyond the range of obtainable thermal population in PL spectra, absorption spectra for the $(\text{Cu-Li})_I$ center are necessary. Since the concentration of the defect binding the exciton under study appears to be rather low, and the oscillator strengths are also weak, the only feasible way of achieving such information is from PLE measurements, employing a cw dye laser. To avoid detection of excitation light, it is in practice necessary to detect a part of the characteristic emission for a particular center, displaced some suitable distance away from the excitation region to be covered. For that reason the $(\text{Cu-Li})_I$ is rather unsuitable for direct PLE measurements, since the phonon-assisted part of the spectrum is too weak (at least in the epilayers). However, in these samples it was possib-

IV DISCUSSION

IV A Electronic structure

The $(\text{Cu-Li})_I$ center has a pair of electronic lines, the one at lowest energy being a magnetic triplet separated from a higher-energy singlet by 1.0 meV. The triplet component has a relatively pure spin character, as can be judged in a magnetic field up to 3.5 T. The splitting is nearly isotropic in the resolution of the Zeeman measurements, with a g value which is close to the electron spin value. The triplet-singlet configuration of the $(\text{Cu-Li})_I$ center therefore corresponds to the BE systems which have been studied for Cu complexes in GaP (10,11) as well as other (Cu-Li) centers in GaP (12,13). In agreement with these BE systems the ODMR measurements confirm the near isotropic behaviour of the triplet states (there are exceptions, however, such as the COL centre which fails to show any ODMR signal (10)). The higher resolution of the ODMR as compared with Zeeman measurements nevertheless reveals the symmetry of the $(\text{Cu-Li})_I$ centre.

The L_I^2 recombination of the $(\text{Cu-Li})_I$ center occurs from a spin-like triplet to a singlet state of a neutral associate, which is iso-electronic with the GaP lattice. According to our observations such a transition is spin-forbidden and therefore strong in PL only when thermally favoured at the lowest temperatures. In magnetic field thermalization is observed between the magnetic subcomponents of this line (Fig. 1). This proves that the splitting takes place in the initial excited state of the exciton, implying that the final state in fact is spin-free. Further evidence for the forbidden nature of this triplet line is the coupling to X-zoneboundary phonon modes which is stronger than for the singlet (Fig. 2). Also it vanishes at temperatures when the highest state becomes thermally populated. Because of the allowed

le to obtain indirectly a (nonselective) PLE-spectrum by detecting the intensity of the deeper $(\text{Cu-Li})_{III}$ spectrum, excited via excitation transfer from $(\text{Cu-Li})_I$ (Fig. 4). The no-phonon transition to the 2.3062 eV triplet ground state is just barely seen below the 2.3072 eV transition. The measured difference in oscillator strength is about a factor 10-15 in favour of the 2.3072 singlet state. In the solution grown samples the intensity of the $(\text{Cu-Li})_I$ luminescence was totally dominating over both $(\text{Cu-Li})_{III}$ and the N exciton lines. In this case a direct selective PLE spectrum was obtainable, though never with strong signal. This spectrum is identical to the nonselective spectrum of Fig. 4 with respect to the $(\text{Cu-Li})_I$ components.

III:C ODMR Results

ODMR experiments have been described many times before and details can be found in Ref. 15. The present measurements were performed at 2K with the sample mounted in either a rectangular microwave cavity operating at 9 GHz or a cylindrical cavity operating at 16 GHz. The luminescence was excited either with 5145 Å or 4830 Å argon ion laser and detected via a monochromator and an S20 photomultiplier. Angular dependence studies of the ODMR resonances at both microwave frequencies showed that these resonances belong to triplet excitons bound at centres with orthorhombic symmetry with principal axes, $x = \langle 211 \rangle$, $y = \langle 011 \rangle$ and $z = \langle 111 \rangle$. The Hamiltonian describing these exciton states in a magnetic field B, is

$$H = \mu_B \underline{S} \cdot \underline{g} \cdot \underline{B} + D (S_x^2 - \frac{1}{3} S(S+1)) + E (S_x^2 - S_y^2)$$

where,

$$S = 1, g_x = 1.98, g_y = 1.93, g_z = 2.00, D = 3.5 \times 10^{-3} \text{ meV},$$

$$E = 5.8 \times 10^{-4} \text{ meV}$$

Full details will be published elsewhere (16).

character of the singlet its lifetime is much shorter and therefore it dominates the radiative recombination. The lifetime of the triplet line is long, on the order of a millisecond. A final evidence is the fact that the triplet component of the BE is very weakly seen in PLE. In contrast to this, the singlet transition occurs between a S=0 magnetic singlet and the spin-free final state of the center. This transition is allowed by the spin selection rule $\Delta S=0$, but the observed lifetime of the transition is 20 μ s which is unusually long compared with similar previously studied transitions.

Spin-forbidden transitions from S=1 BE triplets have been observed in several other cases as mentioned above (10,11,12). A common feature for previously studied singlet-triplet pairs in GaP seems to be the combination of a hole-attractive central cell and a compressive axial crystal field created by the local arrangement of defect atoms. In case of a strong crystal field dominating the relatively small spin-orbit splitting of the valence band of GaP (80 meV), the p-like hole states are split in such a way that an orbital singlet state has the lowest hole energy (10,11). Consequently the BE states are formed through the combination of two spin particles. The sum of two S=1/2 particles results in two BE states with total spin S=0 and S=1. The schematic electronic configuration of such a bound exciton is shown in Fig. 5.

In the (Cu-Li)_I spectrum the triplet BE state has the lowest energy. Assuming that no other correlation terms exist the spacing between the two components is the exchange splitting of the electron and hole of the bound exciton. The energy $\Delta_{\text{exc}} = 1.0$ meV is about the order of magnitude usually found for BE systems in GaP (3). The electronic configuration of the BE states indicates that the dominating central cell of the (Cu-Li)_I defect is hole-attractive. This is in a general agreement with the tentative assumption that the central cell involves the acceptorlike substituent Cu_{Ga} as will be discussed in more detail below under IV B.

IV B. Model discussion of the (Cu-Li)_I center

We recall from the experimental section (Section II) that the doping experiments give no evidence of other impurities than Cu and Li being present in the (Cu-Li) complex. Also the presence of Li is explicitly proved by the isotope shifts of both the significant local modes in the spectrum. The participation of Cu cannot be unequivocally proved by means of isotope doping with Cu, owing to lack of suitable phonon replicas predominantly caused by the motion of Cu alone.

The main reason for assigning the luminescence spectrum described above to a complex involving Cu besides Li is from the doping experiments. We find that the doping procedure always requires a Cu diffusion at high temperatures (900–1100 °C) and a subsequent Li diffusion at lower temperatures, typically 400–650 °C. The (Cu-Li)_I center has never been observed in GaP material which is not deliberately Li doped. Further, in Li doped material which is not previously Cu doped this center is always absent.

The dominant BE spectra in GaP after the Cu diffusion at high temperature have electronic lines at 2.177 eV (10) and 1.911 eV (11). The centers responsible for the Cu luminescence spectra therefore bind the excitons more deeply than is the case for the (Cu-Li)_I center. Both centers have been attributed to complexes containing inequivalent Cu atoms, Cu_i and Cu_{Ga} respectively. The latter is established to have a <100> oriented symmetry axis ascribed to a linear defect of Cu and possibly a native defect such as Ga_i. The 2.177 eV luminescence band shows a complicated phonon coupling to the lattice vibrations suggesting a complex of three Cu atoms. These two Cu-related luminescence bands always vanish as a consequence of the Li diffusion for all diffusion temperatures higher than 350 °C. This is partly a result of the heat treatment caused by the Li-diffusion procedure, (17). In the temperature interval around 250 °C,

Li diffusion produces the $(\text{Cu-Li})_I$ luminescence in coexistence with the COL luminescence. It must be noted that since the $(\text{Cu-Li})_I$ center has a smaller binding energy than either of the Cu-related excitons, the appearance of the former at the same time as the latter ones disappear necessarily implies a reconstruction of the Cu complexes and not a fast excitation transfer to the $(\text{Cu-Li})_I$ center. In agreement with that, no signs of the Cu-related excitons can be seen in the PLE spectra of the Cu-Li codoped samples. (This is also true for the $(\text{Cu-Li})_{III}$ center (12)).

Both the interstitial Cu and Li are highly mobile in the GaP lattice by an interstitial diffusion mechanism. Evidently they are likely to form complexes with substitutional Cu (assumed to exist on Ga sites, ionized at the diffusion temperatures). We argue that the Cu_{Ga} of the $(\text{Cu-Li})_I$ center is most likely to have a d^{10} configuration and consequently forms a complex with two interstitial species to ensure charge neutrality and spin-free ground state of the centre. Strong Auger processes may be expected to compete with the luminescence and shorten its lifetime, in the case of open shell configurations (18). This is in contrast with observations for the $(\text{Cu-Li})_I$ luminescence. Further, there are strong arguments against an unfilled d shell for Cu_{Ga} in GaP, since theoretical calculations place the $\text{Cu}_{\text{Ga}} d^9$ state about 5 eV below the valence band top for GaAs (19).

Hence, we suggest that a neutral isoelectronic centre, involving a substitutional Cu in the d^{10} configuration, is responsible for binding the $(\text{Cu-Li})_I$ exciton. From the isotope doping experiments the associate is known to involve a Li atom. As will be discussed below in Sec. IV.C. the most straight-forward interpretation of the isotope doping is that the $(\text{Cu-Li})_I$ centre involves just one Li atom. However we cannot be definite of this point, and in fact we suggest a defect involving two vibrationally isolated Li_i atoms as one possible identity of the centre, below.

IV C Analysis of local modes

An analysis of local mode energies is a complicated task even in cases where the microscopic identity of the defect is known. In the case of $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_p$ the mixed isotope doping provided evidence for the model of the complex (9). However a detailed calculation was not possible even in this case. It is obvious that a model for the local mode vibration must include the adjustment of force constants that is necessary to reduce the expected local mode energy of Li_{Ga} (110 meV) (9) to the observed energies close to 50 meV. Such an analysis is certainly warranted but will not be attempted at this stage.

Instead, we discuss the most striking features of the local mode structure in relation to possible defect models. There are three usually strong localized modes present in the spectrum. The two local modes show substantial shifts when replacing ^7Li with ^6Li as shown in Table II. The gap mode at 37.7 meV shows no detectable isotope shift, and therefore probably involves a mixed motion of the defect atoms or even pure Cu motion. It is expected that the relative changes in energy with isotope substitution are smaller for gap modes than for local modes, however (9).

In a simple model of the local vibrations the complex is regarded as coupled linear harmonic oscillators centered on each atom in the complex. The atomic masses and the force constants between the atoms are responsible for the energy levels of the harmonic oscillators. In the case of a light atom such as Li one expects high energies of the vibrational quanta and thus localized phonon modes. The energy change $\Delta\hbar\omega$ of a phonon with energy $\hbar\omega$ upon substitution of ^7Li with ^6Li can be expressed as a change in the ion mass ΔM , given that the force constants are independent of the ion mass M :

$$\Delta\hbar\omega = (1/2)\hbar\omega(\Delta M/M)f_{KE}$$

Here f_{KE} is the fractional kinetic energy. The vibration of one

atom is generally not an eigenfunction of the system. The vibrational symmetries can be found from group theory given the microscopic structure of the defect. The system eigenfunctions are linear combinations of the linear harmonic oscillator eigenfunctions of the atoms which depend on the symmetry. The fractional kinetic energy f_{KE} measures how much a given atom takes part in a vibrational eigenfunction of the system. At the same time it gives information on the applicability of this simple model.

The isotope shift of the 52.8 meV mode is $55.6 - 52.8 = 2.8$ meV. Hence we arrive at the value for the fractional kinetic energy $f_{KE} = 0.74$. This is rather low for a local mode, since the value $f_{KE} = 1$, corresponding to a vibration of the Li atom alone, is perhaps expected. For the 51.2 meV mode the isotope shift is $52.4 - 51.2 = 1.2$ meV. Here a fractional kinetic energy $f_{KE} = 0.27$ is deduced, which is a very low value. These values indicate that the local modes do not involve the motion of Li atoms alone.

Two important results from the isotope experiments are crucial for any model of the defect. Firstly we can detect the local modes corresponding to the natural abundance of Li ($92.6\% \text{ } ^7\text{Li}$) in our best spectra. Here we observe about 7% intensity of the 55.6 meV mode relative to the total intensity of the 55.6 and 52.8 meV modes together. This excludes the possibility of two connected Li atoms in the defect since the pure modes should then appear with the relative intensities 0.93^2 and 0.07^2 . The ^6Li mode would indeed be undetectable in this case.

Secondly, we observe no additional local modes for approximately equal amounts of ^6Li and ^7Li in the diffusion source. We only get the pure ^7Li and ^6Li modes simultaneously strong as shown in Fig. 3. This highly inhibits the probability of two or more coupled Li atoms moving either in equivalent or inequivalent sites. In the former case a mixed mode involving ^7Li and ^6Li would appear at an intermediate energy bet-

ween the extreme energies for the pure modes. This mode would be equally strong as both the pure modes together for 50% abundance of each isotope. In case of two inequivalent Li atoms causing the local modes four equally strong modes are expected for equal abundances of each Li isotope. We clearly see nothing of the kind.

To conclude, we state that there is only one Li atom responsible for both local modes of the $(\text{Cu-Li})_I$ spectrum. Any coupled motion of Li atoms in the defect would give rise to modes of mixed isotope motion when both Li isotopes are present in detectable concentrations. The possibility of two vibrationally isolated Li atoms cannot be completely excluded by these arguments. Whether they be on equivalent sites and hence have identical vibronic properties, or completely inequivalent would not be deducible from the data. In the latter case only one of the Li atoms would give rise to both modes, however. A hypothetical configuration for such isolated Li motion would be a pair of interstitial Li atoms, one on each side of the heavier substitutional Cu_{Ga} atom.

The almost identical Li-related local mode structure found for the $(\text{Cu-Li})_{III}$ center (12) was assigned to an interstitial Li atom being bond centred between a Cu_{Ga} substituent and a neighbouring P atom along the $\langle 111 \rangle$ direction. It was suggested that such a configuration would explain the two sharp Li-related local modes as a mixed motion of Li and P atoms, thus accounting for the different isotope shifts observed (12). In view of the similarity between the $(\text{Cu-Li})_I$ and the $(\text{Cu-Li})_{III}$ spectra as far as the local mode structure is concerned it seems natural to assume that both defects involve a Li atom in a similar configuration. Below we arrive at the conclusion that the local mode structure of the $(\text{Cu-Li})_I$ center is caused by a bond centred Li_i atom in agreement with the $(\text{Cu-Li})_{III}$ center (12) (Section IV.D).

IV D. Identity of the $(\text{Cu-Li})_{\text{I}}$ centre

To summarize the discussion so far we have deduced that the $(\text{Cu-Li})_{\text{I}}$ centre is a neutral isoelectronic associate binding an exciton in a magnetic singlet-triplet configuration. The electronic configuration is consistent with an axial hole-attractive defect binding the hole from orbitally nondegenerate valence band states, as a consequence of the compressional sign of the local strain field. The symmetry of the defect is orthorhombic with axes $x = \langle 211 \rangle$, $y = \langle 011 \rangle$ and $z = \langle 111 \rangle$ as revealed by the ODMR measurements. Further, we have shown that the defect contains a Li atom. The isotope doping excludes the possibility of two or more Li atoms in a coupled motion, but if the complex contains more than one Li atom they have to be vibrationally independent of each other.

This accumulated evidence does not lead to an unequivocal model for the identity of the $(\text{Cu-Li})_{\text{I}}$ center. In fact, similar arguments were used to arrive at the proposed model for the $(\text{Cu-Li})_{\text{III}}$ center as a $\langle 111 \rangle$ -oriented $\text{Li}_i\text{-Cu}_{\text{Ga}}$ complex. The Li_i atom was suggested to be bond centred between the substitutional Cu_{Ga} and a neighbouring P host atom, along the $\langle 111 \rangle$ direction (13). This configuration ensures charge neutrality of the $(\text{Cu-Li})_{\text{III}}$ centre, since Cu_{Ga} is a double acceptor and the interstitial atoms are expected to act as single donors in view of their group I character. It was found difficult to fit other neutral configurations along the $\langle 111 \rangle$ axis of the zincblende structure under the above conditions.

Returning to the $(\text{Cu-Li})_{\text{I}}$ center we obviously must suggest an identification which is consistent with the different symmetries of the two complexes and which also accounts for both common features in the two spectra and the differences. Apart from the energy position and the consequences of the shallower binding of the $(\text{Cu-Li})_{\text{I}}$ centre (such as the generally weaker phonon interaction) the main spectral differences seem

to be related to the electronic configuration. There is only one singlet-triplet pair present for the $(\text{Cu-Li})_{\text{I}}$ center, whereas two pairs were observed for the $(\text{Cu-Li})_{\text{III}}$ center. Further, the singlet state of $(\text{Cu-Li})_{\text{I}}$ was found to couple more strongly to the X zone boundary phonons than does its counterpart of $(\text{Cu-Li})_{\text{III}}$. This suggests differences in the local symmetry of the two defects, as resolved in the ODMR measurements.

The striking similarity between the Li-related local modes of the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{III}}$ centres suggests that both involve Li atoms in similar lattice positions. Consequently, we assign the Li-related local modes in the $(\text{Cu-Li})_{\text{I}}$ spectrum to a bond centred interstitial Li atom. The light Li_i atom could distort off the bondcentred position giving the orthorhombic symmetry observed in the ODMR measurements. The choice of a Li_i atom excludes a Li atom on a Ga site, since two nearby Li atoms would give rise to a coupled vibrational motion. We therefore suggest that the hole-attractive Ga-site substitute of the $(\text{Cu-Li})_{\text{I}}$ center is Cu as in the two other most thoroughly studied Cu-Li centers (12,13). As a natural consequence of the above discussion we suggest that the $(\text{Cu-Li})_{\text{I}}$ center is a $\langle 111 \rangle$ -oriented complex composed of $\text{Li}_i\text{-Cu}_{\text{Ga}}$ -D, where D is a single donor. We have tentatively assumed that the $(\text{Cu-Li})_{\text{I}}$ center involves only Cu and Li, because of the lack of correlation with any other dopant in different GaP material. Hence, an interstitial Cu atom or a second interstitial Li atom may be the second donorlike species of the $(\text{Cu-Li})_{\text{I}}$ centre. The two Li atoms in the latter model are inequivalent, since one is bond centred (giving rise to the local modes) and the other occupies an interstitial position of the GaP lattice. Thus the proposed model does not contradict the conclusions from the isotope doping.

If the $(\text{Cu-Li})_{\text{I}}$ center contains two Li atoms behaving as one with respect to the isotope doping, parallels can be drawn with the 969 meV

center in Si (20). Consisting of two substitutional C atoms and a Si atom in a nearby interstitial site between the nearest neighbour C substituents, the C-related local modes have an isotope dependence which is characteristic for only one C atom moving in the vibration (20). If, on the other hand, the second interstitial atom is Cu, the only difference between the $(\text{Cu-Li})_I$ and the $(\text{Cu-Li})_{III}$ centres would be the defect symmetry. It is not possible to say whether a lower symmetry would lead to a decreased binding energy for the $(\text{Cu-Li})_I$ center as compared with the $(\text{Cu-Li})_{III}$ center. This is required, however, if the chemical identities of both centres are identical.

To summarize, we propose that the $(\text{Cu-Li})_I$ center is an orthorhombic $\langle 111 \rangle$ -oriented associate, presumably $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Li}_i$ or $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Cu}_i$. At the present stage it is impossible to distinguish between the two proposed models, however. Although the microscopic models are tentative, it must be noted that both are consistent with all the generic aspects of defects of the class discussed in this paper. They also account for the experimental observations characterizing the $(\text{Cu-Li})_I$ center which were listed at the beginning of this section.

Conclusions

The $(\text{Cu-Li})_I$ center appearing in GaP codoped with Cu (900–1100 °C for 1 hour) and Li (typically 400–600 °C for 40 minutes) has been studied by photoluminescence techniques via the bound exciton spectrum associated with the center. A model for the identity of the center is deduced from the doping procedure employed, the electronic structure of the exciton bound by the center and details in its vibrational sidebands.

The electronic configuration of the $(\text{Cu-Li})_I$ bound exciton is a magnetic triplet at 2.3062 eV and a singlet at 2.2072 eV, separated from the triplet by an electron-hole exchange splitting of 1.0 meV. The

centre binding this exciton is a neutral associate of isoelectronic molecular type. This identification is based on the requirement of a neutral and spin-free final state of the BE recombination for a singlet-triplet pair of BE states to occur. Moreover, a thermalization between the magnetic subcomponents of the triplet in a magnetic field in PL measurements shows that the splitting occurs in the initial state of the BE recombination. An additional requirement for the observed electronic configuration is that the orbital angular momentum of the involved hole states is quenched in the local axial strain field. The strain field must necessarily have a compressional sign. The magnetic triplet state of an exciton formed under such conditions should split almost isotropically in magnetic field. This is indeed observed for the $(\text{Cu-Li})_I$ bound exciton. The slight anisotropy present in the triplet splitting has been resolved by the ODMR technique, which reveals an orthorhombic symmetry with a $\langle 111 \rangle$ z-axis for the $(\text{Cu-Li})_I$ center. This information was obtained from the angular dependence of typical triplet resonances in the ODMR signal (16).

The chemical identification of the $(\text{Cu-Li})_I$ center is based on the doping procedure, which always requires Cu doping prior to the Li doping for the BE spectrum to appear. The presence of Li in the defect associate is also explicitly proved by the Li-isotope doping. Well resolved shifts of the local mode energies are caused by the substitution of ^7Li by ^6Li . We also find that the 55.6 meV local mode appears with an intensity ratio corresponding to the natural abundance of ^6Li when doping with natural Li metal (92.6 % ^7Li , 7.4 % ^6Li). Further, we find that doping with approximately equal amounts of both Li isotopes introduces no modes of mixed-isotope vibrations. The Li-isotope doping excludes the possibility that the local modes are caused by a coupled motion of two or more Li atoms. If the defect complex contains more than one Li atom these must be vibrationally independent of each other. From

the compiled information on the $(\text{Cu-Li})_I$ center we propose a model for its identity as an associate consisting of $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Li}_i$ or $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Cu}_i$ along the $\langle 111 \rangle$ direction. The two Li atoms of the former configuration are inequivalent, since the first one is suggested to be bond-centred between a Cu_{Ga} substituent and a nearest neighbour P host atom, whereas the second one occupies an interstitial lattice position.

The bond-centred Li atom is proposed to be distorted off the $\langle 111 \rangle$ direction, thus giving the orthorhombic symmetry. Both Li-related local modes in the $(\text{Cu-Li})_I$ spectrum are ascribed to the bond-centred Li_i atom.

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References

1. S.T. Pantelides, *Rev. Mod. Phys.* **50**, 797 (1978)
2. J.A. van Vechten in *Handbook of Semiconductors*, Vol. 3, *Materials, Properties and Preparation*, Ed. S.P. Keller, (North Holland, Amsterdam 1980) Ch.1.
3. P.J. Dean and D.C. Herbert in *Topics in Current Physics*, Vol. 14, *Excitons*, Ed. K. Cho (Springer, Berlin 1979) pp 55-182
4. T.N. Morgan, B. Welber and R.N. Bhargava, *Phys. Rev.* **166**, 751 (1968)
5. C.H. Henry, P.J. Dean and J.D. Cuthbert, *Phys. Rev.* **166**, 754 (1968)
6. E. Cohen and M.D. Sturge, *Phys. Rev. B* **15**, 1039 (1977)
7. J.J. Hopfield, D.G. Thomas and R.T. Lynch, *Phys. Rev. Lett.* **17**, 312 (1966)
8. J. van W. Morgan and T.N. Morgan, *Phys. Rev. B* **1**, 739 (1970)
9. P.J. Dean, *Phys. Rev. B* **4**, 2596 (1971)
10. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, *Phys. Rev. B* **25**, 7719 (1982)
11. H.P. Gislason, B. Monemar, P.J. Dean, D.C. Herbert, S. Depinna, B.C. Cavenett and N. Killoran, *Phys. Rev. B* **26**, 827 (1982)
12. H.P. Gislason, B. Monemar, M-E. Pistol, P.J. Dean, D.C. Herbert, S. Depinna, A. Kana'ah and B.C. Cavenett, manuscript
13. H.P. Gislason, M-E. Pistol, B. Monemar, A. Kana'ah and B.C. Cavenett, manuscript
14. P.J. Dean, *Proc. Int. Conf. on Luminescence*, Leningrad 1972, Ed. F. Williams (Plenum Press, 1973) p.538
15. B.C. Cavenett, *Advances in Physics* **30**, 475 (1981)
16. A. Kana'ah, B.C. Cavenett, H.P. Gislason, M-E. Pistol and B. Monemar, manuscript
17. G.M. Blom and R.N. Bhargava, *J. Crystal Growth* **17**, 38 (1972)
18. D.J. Robbins and P.J. Dean, *Advances in Physics* **27**, 499 (1978)

19. L.A. Hemstreet, Phys. Rev. B22, 4590 (1980)
20. G. Davies, E.C. Lightowler and M.C. do Carmo, J. Phys. C 16, 5503 (1983)

Table 1. Photon energies of the electronic transitions in the (Cu-Li)_I photoluminescence spectrum. The energies of the most significant phonon replicas of L_I¹ and L_I² are listed in separate columns.

Notation	Photon energy eV	Energy from L _I ¹ meV	Energy from L _I ² meV	Interpretation
L _I ¹	2.3072	0		S = 0 singlet
L _I ²	2.3062	1.0	0	S = 1 triplet
	2.2941	13.1		TA ^x
	2.2931		13.1	TA ^x
	2.2768	30.4		LA mode
	2.2746		31.6	LA ^x
	2.2695	37.7		Gap mode
	2.2685		37.7	Gap mode
	2.2620	45.2		TO ^x
	2.2610		45.2	TO ^x
	2.2615	45.7		TO ^r
	2.2605		45.7	TO ^r
	2.2570	50.2		LO ^r
	2.2560		50.2	LO ^r
	2.2550	51.2		Local 7 _{Li} mode
	2.2548	52.4		Local 6 _{Li} mode
	2.2538		52.4	Local 6 _{Li} mode
	2.2544	52.8		Local 7 _{Li} mode
	2.2534		52.8	Local 7 _{Li} mode
	2.2516	55.6		Local 6 _{Li} mode
	2.2506		55.6	Local 6 _{Li} mode

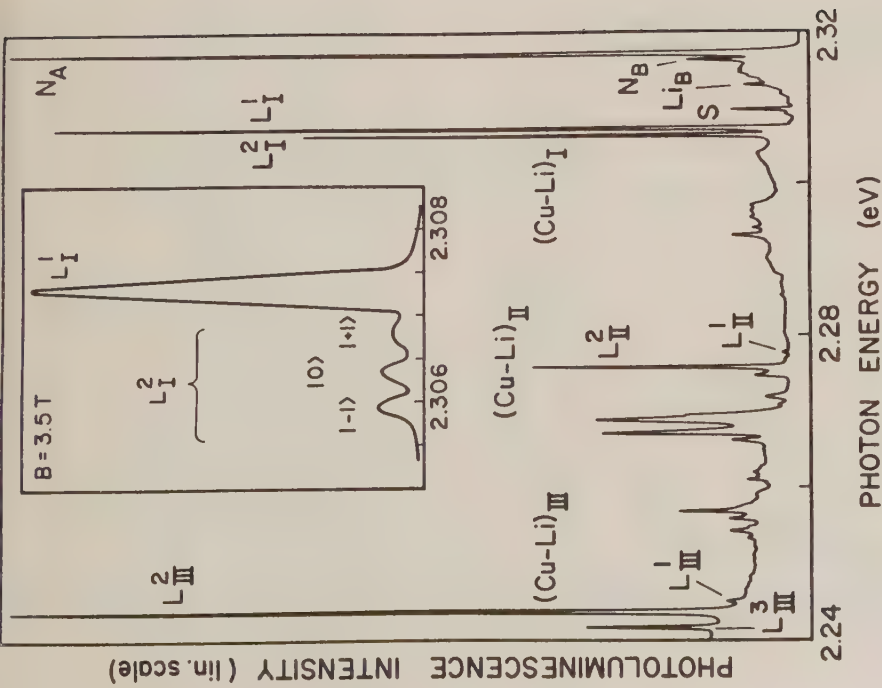


Fig. 1 Low temperature PL spectrum of an epitaxial GaP wafer diffused with Cu and Li and excited with the 5145 Å Ar⁺ laser line. The group of electronic lines labelled (Cu-Li)_I are consistently present in this type of material after such doping. In the inset the electronic lines of the (Cu-Li)_I spectrum are shown in magnetic field B = 3.5 T. The L_I^1 line does not split while the L_I^2 line splits into three magnetic subcomponents, corresponding to an isotropic g value.

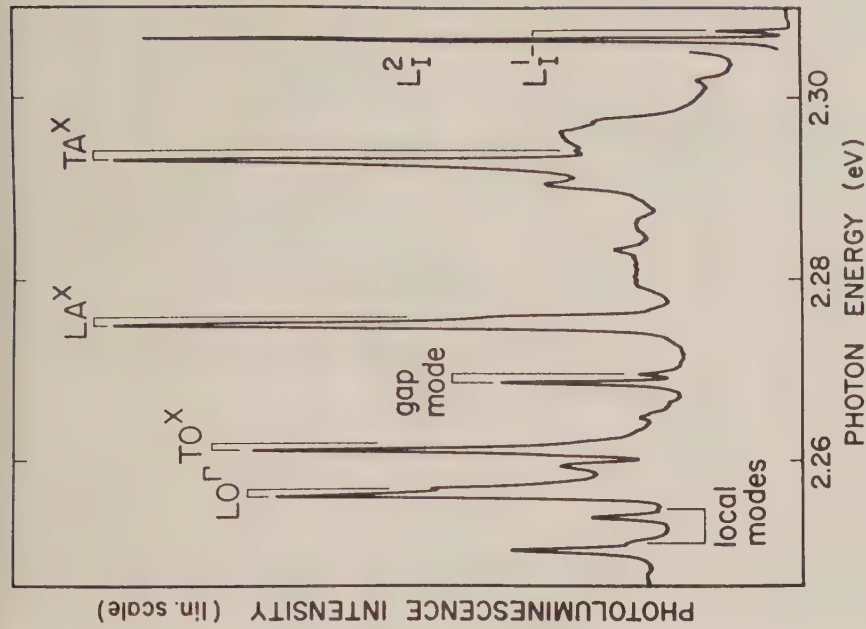


Fig. 2a The low-temperature PL spectrum of a solution grown GaP sample doped with Cu and Li. Below 2K, thermalization favours the spin-forbidden L_I^2 transition which dominates in this spectrum. The phonons at the X-point of the Brillouin zone show a strong coupling to this forbidden line, as does LO_I^+ . Note in particular the strong localized modes present in the (Cu-Li)_I spectrum. Both a sharp gap mode of 37.7 meV is found as well as two distinguished true local modes. This crystal was doped with the 6Li isotope.

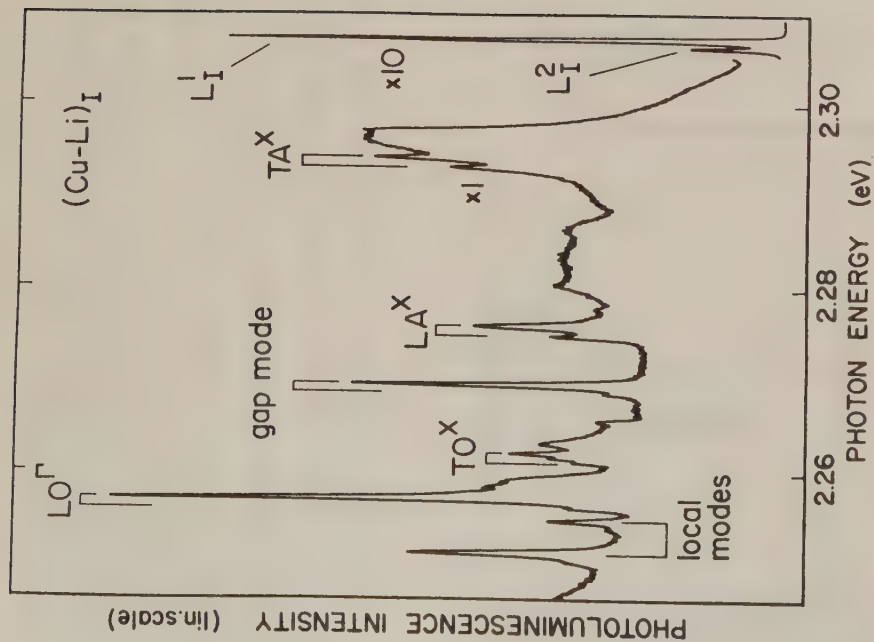


Fig. 2b PL spectrum of the same crystal as in Fig. 2a at a slightly higher temperature. Here the electronic singlet state is thermally populated and the L_1^1 singlet transition dominates due to the forbidden character of the triplet L_1^2 . Observe that the LO^Γ shows similar coupling strengths to both electronic components. This is also the case for all localized phonon modes. The zone boundary phonons, on the other hand, clearly couple more strongly to the triplet line.

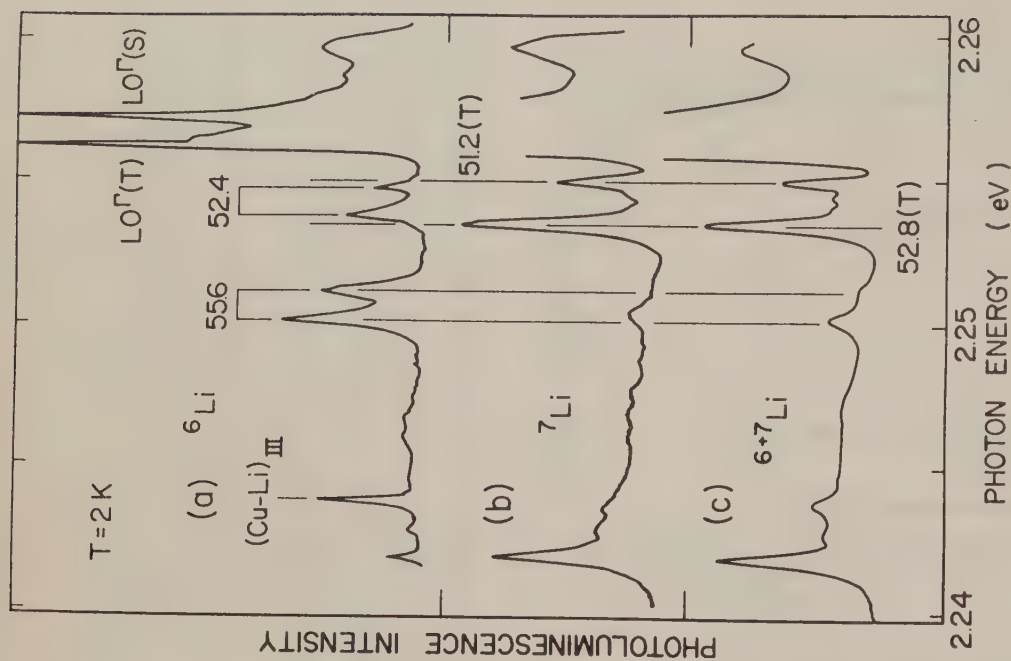


Fig. 3a Portion of the low temperature PL spectrum of $(Cu-Li)_I$ showing the true local modes for samples doped with the 6Li isotope

(curve a) natural Li with 92.6% 7Li abundance (curve b) and approximately equal amounts of both Li isotopes (curve c). 7Li gives rise to two discrete local modes at 51.2 and 52.8 meV, respectively. Note that a weak peak corresponding to the natural abundance of 6Li (7.4%) appears in the spectrum for natural Li (curve b). The mixed isotope doping (curve c) shows no new modes but only confirms the result from the natural Li with different relative isotope abundance.

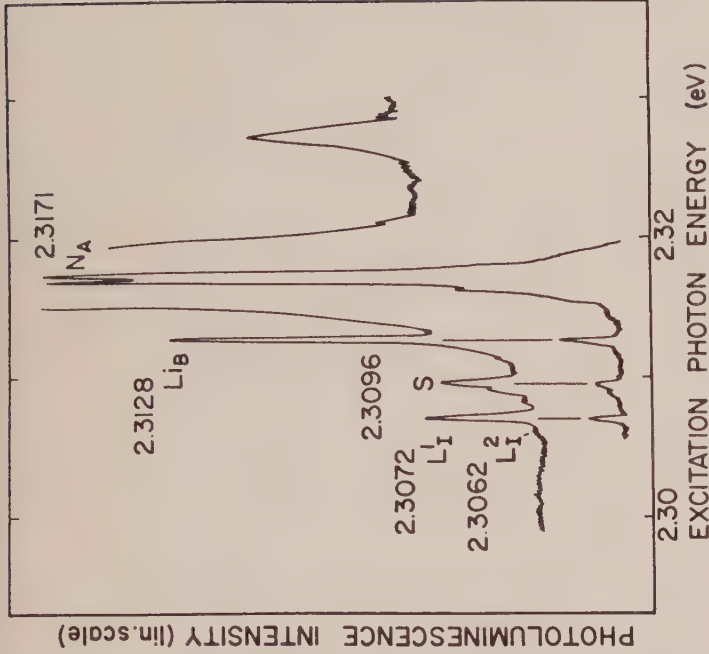


Fig. 4 Low temperature PL spectrum of the $(\text{Cu-Li})_{\text{I}}$ BE monitoring the $(\text{Cu-Li})_{\text{III}}$ PL. The spectrum was measured with a tunable dye laser excitation using the same epitaxial wafer as in Fig.1. In this kind of sample selective detection of the $(\text{Cu-Li})_{\text{I}}$ luminescence was not possible owing to weak phonon sidebands. Detection was instead made possible through excitation transfer to the $(\text{Cu-Li})_{\text{III}}$ spectrum. The spinforbidden triplet L_2^2 is very weak while the singlet L_1^1 is stronger. Other well known BE:S in GaP are observed through a similar excitation transfer to $(\text{Cu-Li})_{\text{III}}$. Observe that LiB is strong whereas no sign of LiA is seen in PL of PL spectra. The peak at 2.328 eV is related to the pronounced N bound exciton.

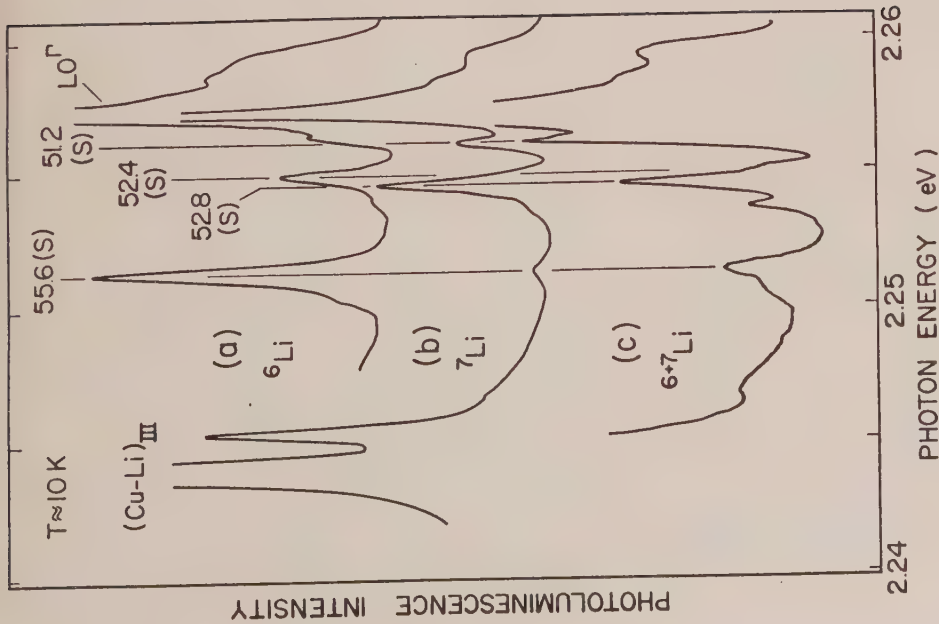


Fig. 3b The same portion of the $(\text{Cu-Li})_{\text{I}}$ PL spectrum at higher temperature than in Fig. 3a. Here the singlet transition L_1^1 dominates and consequently its replicas are strong. Owing to the closely spaced local mode replicas of $(\text{Cu-Li})_{\text{I}}$ it is necessary to register intensity variations of the replicas with temperature in order to sort out the modes correctly.

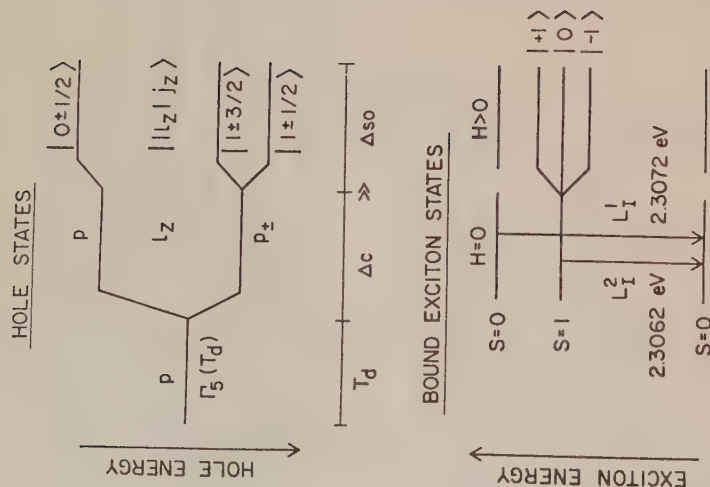


Fig. 5 A schematic level diagram showing the generic model for exciton binding at hole-attractive neutral defects in axial symmetry. The orbitally threefold degenerate hole states split in a compressive axial strain field that exceeds the spin-orbit interaction of the host lattice. The ground state of the holes is the orbitally nondegenerate $|0 \pm 1/2\rangle$ state in the $|1 l_z | j_z\rangle$ notation after spin-orbit coupling. When this hole state couples to a similarly nondegenerate electron spin state, the bound exciton states have the spin-only-like singlet-triplet configuration $S=0$; $S=1$. Thermalization within the magnetic subcomponents in a magnetic field reveals whether the splitting occurs in the initial or final state of the transition. The former case is observed here in agreement with this scheme.

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Abstract

A photoluminescence study is reported in order to identify a new radiative center in GaP codoped with Cu and Li. This center, denoted (Cu-Li)_{III}, binds an exciton with binding energy 110 meV. The bound exciton spectrum shows sharp electronic lined and a structured phonon sideband with well resolved replicas. The group of electronic transitions consists of spin-only-like singlet-triplet pairs, which are characteristic of tightly bound holes in a strong compressive axial crystal field. Two such singlet-triplet pairs are observed for the (Cu-Li)_{III} center, instead of usually one pair. A model taking into account the splitting of electron states as well as hole states is proposed to explain this additional splitting. The experimental work includes photoluminescence spectroscopy, time resolved and Zeeman measurements as well as optically detected magnetic resonance measurements. The careful doping procedure includes isotope doping with both ⁶³Cu, ⁶⁵Cu and ⁶Li, ⁷Li. The Li-isotope doping was clearly reflected in the phonon sideband. A neutral molecular associate of isoelectronic nature is suggested, the identity of the (Cu-Li)_{III} center, is involving Cu_{Ga} and a pair of interstitial atoms, Cu_i and Li_i.

1. Introduction

Isoelectronic centers occur not only as simple, single substitutional impurities, but also as associated donor-acceptor pair complexes. Such electrically neutral complexes are easily formed during diffusion at high temperatures due to Coulomb attraction between species of opposite charge (1).

A small but significant proportion of neutral associate centers causes a perturbation strong enough to bind excitons with associated sharp-line photoluminescence spectra at low temperature. The Hopfield-Thomas-Lynch (HTL) model for isoelectronic point defects in semiconductors has successfully been extended to electron-attractive associate defects, such as nitrogen pairs in GaP where the separation of the atoms is much less than the Bohr radius of the exciton (2).

Recently, there has been growing interest in the hitherto neglected case of neutral complexes dominated by acceptor-like central cells. A generic model for such defects, accounting for the splitting of the tightly hole states in the reduced symmetry, has been discussed previously (3,4). The model has been used to explain the electronic structure of excitons bound to complexes of Cu in GaP. These excitons are subject to a strong axial field which causes a large binding energy for the electron as well as the hole, and consequently, a large electron-hole exchange interaction. Hence, the HTL model is not applicable to these bound exciton systems.

New Cu-Li centers appear as a result of a Li diffusion of the Cu-doped samples. Both these dopants are fast interstitial diffusers and being singly ionized at the diffusion temperature they are expected to be attracted by either Li_{Ga} or Cu_{Ga} . Neither of these substitutional impurities has been positively identified, but at least 5 complexes involving Cu and Li in GaP have been observed in BE spectra so far (5,6,7). In a separate paper (5) we have reported on a center denoted as $(\text{Cu-Li})_{\text{I}}$ with a lowest bound exciton line at 2.306 eV. Another defect, referred to as the $(\text{Cu-Li})_{\text{V}}$ center binding an exciton at 2.172 eV will be discussed in a forthcoming paper (6). The $(\text{Cu-Li})_{\text{III}}$ complex discussed in the present paper binds an exciton with the lowest electronic transition at 2.242 eV

In Section II we describe the doping procedure necessary to produce a strong $(\text{Cu-Li})_{\text{III}}$ luminescence. Also, we outline the experimental techniques used in the optical measurements. In Section III A we present photoluminescence (PL) data for this center, including spectra measured in a magnetic field of 6T. In Section III B we describe the results from the Li-isotope doping, in Section III C results from photoluminescence excitation (PLE) measurements are given, and in Section III D the optically detected magnetic resonance (ODMR) data are summarized. In the discussion section (Section V) we correlate the observations with a model for the electronic structure as well as a possible structural model of the defect. We pay particular attention to the results of the Li-isotope doping, which causes substantial shifts of the local mode replicas in the strong phonon sideband of this defect.

II. Experimental

A. Sample preparation

The Cu and Li doped GaP samples were prepared from epitaxial (LPE) wafers, solution grown material, and Czochralski bulk material (LEC). The starting material was either n-doped, P-doped or nominally undoped. It was found that the $(\text{Cu-Li})_{\text{III}}$ spectrum is most easily produced in the purest starting material. It was found necessary to diffuse the samples in two steps. First a Cu diffusion was made at high temperature with a subsequent Li diffusion at lower temperatures. The reverse order produced no Cu-Li spectra. Li doping alone only caused the shallow Li_A and Li_B excitons to appear (8) along with the corresponding shallow DA pair emissions.

The Cu diffusion was performed in the temperature range 900–1100°C for one hour. The samples were diffused in an evacuated quartz ampoule. All samples were quenched in water to room temperature. This procedure, which has been described elsewhere (3) gives rise to the characteristic orange Cu luminescence (COL) at 2.177 eV. Separately we prepared samples with both ^{63}Cu and ^{65}Cu isotopes.

The Li diffusion step was performed at 400–1000°C for 40 minutes to 4 hours in an evacuated quartz ampoule. A pellet of natural Li metal (92.6% ^7Li , 7.4% ^6Li) was placed in the ampule. Separately, crystals were diffused with the ^6Li isotope and with a mixture of approximately equal amounts of ^6Li and ^7Li . The natural Li metal represented the ^7Li isotope.

After the Li doping in this temperature interval the COL luminescence always disappears completely. At the same time several new spectra appear. At least three of these appear regularly ((Cu-Li) $_{\text{I}}$ (5), (Cu-Li) $_{\text{II}}$ and (Cu-Li) $_{\text{V}}$ (6)) with relative intensities depending on starting material and diffusion procedure.

The (Cu-Li) $_{\text{III}}$ luminescence is strongest in nominally undoped epitaxial samples, Li-diffused at 600°C for 1 hour. This spectrum is also easily produced in solution grown material, at lower Li diffusion temperatures for longer times, typically 400°C for 4 hours. However the (Cu-Li) $_{\text{I}}$ luminescence at 2.306 eV always dominates in the solution grown samples (5). It was found that only the purest bulk material was useful for studying the (Cu-Li) $_{\text{III}}$ luminescence. The spectra are generally broader in the bulk material and in the region 2.17–2.25 eV donor acceptor pair (DAP) spectra usually appear in GaP unless very pure.

In bulk material a third center (Cu-Li) $_{\text{V}}$ was easily produced at lower Li diffusion temperatures with longer diffusion times. In nominally undoped samples it was found that the relative strength of the (Cu-Li) $_{\text{III}}$ luminescence increased as the Li diffusion temperature increased from 400°C–800°C with a corresponding decrease of the diffusion time in order to avoid damage of the sample surface.

We found no correlation between the (Cu-Li) $_{\text{III}}$ center and other dopants often present in the samples. The most abundant ones were N,S,O,Te,S,Zn and Ba, which could often be detected in the samples through their corresponding bound excitons.

II. B. Experimental Techniques

Photoluminescence (PL) measurements were performed with Art cw laser excitation at 5145 Å with typical intensity 100 mW. The sample temperature could be varied from 1.8 K to room temperature. The PL spectra were recorded through a Jarrell Ash 0.75 m double grating monochromator employing a Nicolet 1170 signal averager. The magneto-optical experiments were made at the University of Hull with a superconducting magnet at fields up to 6T. The lifetime measurements were made at RSRE using cathodoluminescence and at Hull University with conventional pulsed laser measurements as well as frequency response spectroscopy measurements. Optically detected magnetic resonance results were obtained at a microwave frequency of 9 GHz using a superconducting magnet system (9). The microwaves were chopped at approximately 300 Hz. The luminescence in the ODMR measurements was also excited at 5145 Å. The luminescence intensity changes were measured either for all light or selected wavelengths using a suitable choice of band pass filters or a monochromator. An S20 photomultiplier was used for photoluminescence detection.

Photoluminescence excitation measurements used cw dye laser excitation with narrow band detection through the Jarrel Ash monochromator. The signals were extremely weak. Broad band detection, collecting the whole of the luminescence, did not improve the signal to background ratio.

III. Experimental results

III. A. Photoluminescence spectra

In Fig. 1a a typical low temperature PL spectrum is shown for a Cu-Li codoped epitaxial wafer. Three independent BE spectra are observed in Fig. 1, labelled $(\text{Cu-Li})_{\text{I-III}}$. The $(\text{Cu-Li})_{\text{I}}$ center is described elsewhere (5), while the $(\text{Cu-Li})_{\text{II}}$ spectrum has not been investigated in detail, since it is usually weak.

The $(\text{Cu-Li})_{\text{III}}$ PL spectrum exhibits four electronic lines as shown in Fig. 2. The lowest line L4^0 occurs at 2.2419 eV, and it has a small relative oscillator strength. Therefore it is strong only when thermal-ly favoured at the very lowest temperatures (Fig. 2a). The other two lines appear at 2.2440 eV (L2^0), and at 2.2454 eV (L1^0 , Fig. 2c). A close inspection in high resolution (Fig. 2d) reveals a weak component between the L4^0 and L2^0 lines. This line is denoted L3^0 and is always of negligible strength in our spectra. The L4^0 line is a magnetic triplet according to Zeeman measurements up to 6T. This is shown in the inset of Fig. 1, where the lowest magnetic subcomponent is strongest due to thermalization. Neither L2^0 nor L1^0 splits in a magnetic field of 6T. The decay time for the L4^0 triplet is very long, about 500 μs , where as the singlet L2^0 has a decay time of about 5 μs , also unusually long.

The phonon coupling to the $(\text{Cu-Li})_{\text{III}}$ center is stronger than for more shallow centers such as $(\text{Cu-Li})_{\text{I}}$ (5), and it is different for the different electronic states. This is illustrated in Fig 3 as well as in Table I, which contains a list of all phonon replicas observed in the $(\text{Cu-Li})_{\text{III}}$ spectrum. The phonon coupling of L4^0 is characterized by three sharp peaks at the energies of the dominant phonons close to the X point of the Brillouin zone in the GaP reciprocal lattice (10). They are L4^{TA} ($\text{TA} = 13.2$ meV), L4^{LA} ($\text{LA} = 31.5$ meV) and L4^{TO} ($\text{TO} = 45.3$ meV). In addition, coupling of L4^0 to LO^{T} is represented by a peak L4^{LO} at phonon energy 49.9 meV.

The most striking difference in the phonon coupling to the L4^0 triplet and the L2^0 singlet is that the strong zone boundary phonon replicas TA^{X} , LA^{X} and TO^{X} observed in the phonon sideband of L4^0 are virtually absent for L2^0 . The LO^{T} interaction is of similar strength for both states, however, as evidenced in Fig. 3.

It was difficult to study the phonon coupling to the highest $(\text{Cu-Li})_{\text{III}}$ singlet state L1^0 in detail, but the absence of strong coupling to the X-zone boundary phonons indicates a similar phonon coupling as to the L2^0 line.

III. B. Isotope measurements

Fig. 4 shows in detail the two local modes in the $(\text{Cu-Li})_{\text{III}}$ spectrum, a rather strong one at 53.3 meV and a weaker one at 57 meV for ^7Li , and at 56.8 meV and 60 meV respectively for ^6Li . The abundances of ^6Li and ^7Li were approximately reflected in the relative intensities of the local modes after doping with natural Li, indicating that there is only one Li atom vibrating in the $(\text{Cu-Li})_{\text{III}}$ center. Similar but better resolved local mode spectra were obtained for the $(\text{Cu-Li})_{\text{I}}$ center (5).

Mixed isotope doping using approximately equal amounts of ^6Li and ^7Li in the ampoule reveals no new peaks. As will be discussed below the simplest interpretation of these results is a model of the $(\text{Cu-Li})_{\text{III}}$ center involving only one Li atom.

III. C. PLE measurements

The broad phonon wing in the PL spectrum of the $(\text{Cu-Li})_{\text{III}}$ center allows a direct detection of PLE spectra. The result of such a measurement is shown in Fig. 5. A strong background from dominant exciton or carrier capture via two step excitation had to be subtracted in the figure in order to display the weak signal.

Three strong transitions are positively identified in the PLE spectrum of Fig. 5. The two lines A1^0 at 2.2454 eV and A2^0 at 2.2440 eV correspond to the two singlets L1^0 and L2^0 , respectively. The transition to the weak magnetic triplet ground state at 2.2419 eV does not appear in the PLE spectrum, neither is the second triplet state L3^0 observable.

In addition to these lines a sharp line appears in the PLE data at 2.2510 eV. This line is 9 meV above L4^0 and thus never thermally populated in PL measurements. We do not know whether it belongs to the $(\text{Cu-Li})_{\text{III}}$ center or to another unidentified center. A slightly wavy background is present in the PLE spectrum from stray light, but LA and TA density-of-states maxima are identified.

III. D. ODMR measurements

The optically detected magnetic resonance results will be published in detail separately (11) and so only a brief summary will be given here. The ODMR results for the $(\text{Cu-Li})_{\text{III}}$ centre confirm triplet excitation recombination at axial centres and the symmetry of the centres as $\langle 111 \rangle$ was deduced by detailed angular dependence measurements of the ODMR signals fitting the data into the well known spin Hamiltonian

$$H = \mu_B \underline{S} \cdot \underline{g} \cdot \underline{B} + D (S_z^2 - \frac{1}{3} S(S+1))$$

where: $S = 1$, $g_{\parallel} = 2.00$, $g_{\perp} = 1.95$ and $D = 0.04 \text{ cm}^{-1}$.

IV. Discussion

IV. A. Electronic structure of the $(\text{Cu-Li})_{\text{III}}$ bound exciton

The $(\text{Cu-Li})_{\text{III}}$ center is characterized by a set of four electronic BE lines. The lowest line L4^0 is a magnetic triplet with $g \approx 2$. The weak component L3^0 is never strong in PL and not detectable in PLE, which suggests a forbidden triplet configuration. Both high energy components, L2^0 and L1^0 , are singlets. The lowest singlet-triplet pair, L4^0 , L2^0 of this BE has a JJ-splitting of 2.1 meV, which is about the order of magnitude usually found in GaP (1,7). The second pair, L3^0 , L1^0 has a similar JJ-splitting.

A common feature for previously studied BE singlet-triplet pairs is the combination of a dominating central cell, attractive for holes, and a strong compressive strain field from the local arrangement of the

defect atoms (2,4,5). This field splits the hole states, giving the observed BE states through a combination of two spin ($S=1/2$) particles- (3,4,5). In this scheme transitions between the $S=0$ ground state and the triplet are forbidden by the spin selection rule $\Delta S=0$. When the triplet is heavily favoured by thermalization at low temperatures, transitions violating this selection rule are observed. This was first realized in the study of Cu-related defect in GaP (3,4,5).

The $(\text{Cu-Li})_{\text{III}}$ spectrum differs from other Cu and Cu-Li related spectra since it involves two singlet-triplet pairs of BE states instead of only one. We present here a generic scheme for the formation of two pairs of singlet-triplet BE states and propose an explanation for the $(\text{Cu-Li})_{\text{III}}$ center in this scheme.

In Fig. 6 we summarize the effect of a compressive axial crystal field on the p-like hole states derived from the topmost valence band of GaP. The crystal field splitting is assumed to be large, exceeding the spin-orbit splitting of GaP. A necessary condition for this is that the hole wavefunction is localized at the defect. Therefore the hole must be tightly bound by an overall hole-attractive associate center. The ground state of the holes is then the orbital singlet $||1_z|j\rangle = |0 \pm \frac{1}{2}\rangle$. It will be at lowest energy only for a compressive sign of the crystal field (12). If the electron wavefunction were orbitally nondegenerate there would be a single singlet-triplet pair. The possibility of two such pairs is based on the fact that the lowest electron state may be multivalley degenerate. Then a local stress can cause an additional splitting of the BE states. This requires a non-attractive central cell for electrons (13).

GaP is an indirect semiconductor with a set of equivalent conduction band minima near the X point of the Brillouin zone. It is well known that the pseudopotential difference between Ga and P splits the X minima into X_1 and X_3 subminima (14). (The camel's back structure is omitted in this description.) Depending on the origin of coordinates, the lower conduction band is labelled X_3 (Ga-site) or X_1 (P-site) (15). For electrons bound at the electron-attractive group V sites the 1s ground state derived from the X_1 minima splits into a lowest $1sA_1$ state and a higher $1sE$ state by the valley-orbit splitting. With spin included, the notations are Γ_6 and Γ_8 , respectively, in cubic symmetry.

For electrons bound at the less electron-attractive group III site the wavefunction possesses nodes in the Bloch component instead of antinodes on the group V sites. Therefore the orbitally threefold degenerate $1sT_2$ ground state derived from the X_3 conduction band minima is unaffected by the valley-orbit splitting. When spin is included a Γ_7 ground state and a higher Γ_8 state result (this spin-valley interaction is likely to be negligible feature for a strong axial field). The orbital degeneracy of the Γ_8 electron state can be lifted in a uniaxial strain field. For a direction of the axial field other than $\langle 111 \rangle$ the state splits into two spin doublets, since the equivalence of the conduction band valleys is destroyed. Only the $\langle 111 \rangle$ direction is equivalent for the set of $\langle 100 \rangle$ conduction band minima.

The $(\text{Cu-Li})_{\text{III}}$ associate center is likely to be dominated by a hole-attractive Ga-site substituent with local symmetry reduced by interstitial Cu or Li atoms giving charge neutrality at the defect. The trigonal symmetry of the $(\text{Cu-Li})_{\text{III}}$ defect is not expected to split the electron states. However, if a small perturbation is superimposed on

the major trigonal strain field a small splitting of the multivalley degenerate electron states may be produced. The magnitude of such a strain field component should be much smaller than the strain field acting on the above mentioned Cu defects. (In fact such a component was not resolved in the ODMR data (11)). Two closely spaced Γ_6 orbital singlets will result in this model (as well as a Γ_4 , Γ_5 orbital singlet at higher energy), as schematically illustrated in Fig. 6. We propose that the observed two sets of singlet-triplet BE states result upon taking the triplet product of the symmetric envelope functions, the nondegenerate hole state and the pair of Γ_6 orbital singlet electron states (13).

Thus, we argue that the singlet-triplet pair $L4^0$ and $L2^0$ derive from the lowest electron state while the $L1^0$ state is the singlet component of a second pair $L1^0$, $L3^0$ resulting from a higher, moderately split off electron state. The $L3^0$ component is shown to the right in Fig. 7 characterized with a broken arrow. We have no explanation for the fifth line which appears in PLE measurements at 2.2510 eV. In this scheme, possible explanations are split-off hole states and higher electron states. In the absence of magento-optical data on this component we do not speculate further in its origin.

IV. B. Models for the identity of the $(\text{Cu-Li})_{\text{III}}$ center

The different experimental results from this study do not result in an unequivocal microscopic model of the $(\text{Cu-Li})_{\text{III}}$ center. Nevertheless, we propose a model of the defect from the existing data, considering different possibilities.

The observed magnetic multiplicity of the BE lines is consistent with spinfree final states of the PL emission. A model of two or more particles in the ground state pairing off to give $S=0$ is not attractive due to strong Auger processes, which should severely weaken the corresponding luminescence. For the same reason complexes containing a Cu atom with an open d-shell configuration seem improbable (16). The long radiative lifetime of this BE luminescence further supports the hypothesis of an isoelectronic molecular center, with no electronic participation in the ground state (17).

Both the group I interstitial species Li and Cu are expected to act as single donors. As substitutional ions on Ga sites both would be double acceptors, but neither of these has so far been identified to exist isolated. Both Li_{Ga} and Cu_{Ga} are, on the other hand, found as parts of complexes, such as $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_p$ (7) and the COL complex (3).

Given the diffusion procedure described above, several possibilities for forming neutral complexes of Cu and Li atoms exist. Either Cu or Li may occupy a Ga site to provide the hole-attractive central cell of the $(\text{Cu-Li})_{\text{III}}$ complex. The mobile Li_i^+ donors (ionized at the diffusion temperatures) may combine with a charged acceptor-like complex of Cu atoms influenced by the Coulomb attraction. Similarly the Cu_i^+ donors may pair with an acceptor-like Li complex.

It is evident that the Li isotope experiments are consistent with one Li atom present in the complex. If the local modes result from a coupled motion of more than one Li atom modes of mixed Li isotopes would be reflected in the spectrum. If there are two coupled Li atoms in a defect, either on equivalent sites or not, combinations of both isotopes result in three or four modes, respectively. The above mentioned arguments are not valid if the complex involves inequivalent uncoupled Li atoms. For these reasons we cannot completely rule out the possibility of more than one Li atom in the complex.

For the $(\text{Cu-Li})_{\text{III}}$ complex we favour a model involving Cu_{Ga} acceptor-like central cell and tentatively assign this center to a neutral complex of $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Cu}_i$. In the $\langle 111 \rangle$ direction in a zincblende lattice there are two adjacent interstitial sites, a cubic and a hexagonal one (18). Since it may be unlikely that both the donor-like species of the complex sit on the same side of the acceptor-like species, we propose that there is a bond-centered unbonded Li_i present on one side of Cu_{Ga} while the second interstitial (presumably Cu_i) occupies either of the interstitial sites. We believe that a slight perturbation of the trigonal symmetry caused by a small relaxations off the linear configuration would be sufficient to explain the splitting of the electronic states suggested in Section IV A.

We consider a model involving Li_{Ga} unlikely. Two Cu_i (instead of a Cu_i and a Li_i) would then be needed for reasons of charge neutrality, since a $\text{Li}_{\text{Ga}}\text{-Li}_i$ pair would certainly be expected to give rise to coupled vibration of Li atoms, as in the $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_p$ system (7). A bond centered Cu_i (would be necessary in view of the $\langle 111 \rangle$ orientation) may be more difficult to realize owing to the large radius of Cu_i , even though such a configuration may be probable for the smaller Li_i .

IV. C. Symmetry and origin of the local modes

From figures 3 and 4 we note the important fact that both local modes in the $(\text{Cu-Li})_{\text{III}}$ spectrum couple equally strongly to the electronic singlet and triplet lines. The LO^Γ phonon has a similar coupling to both components while the transverse phonons TA^X , LA^X and TO^X all show

a strong coupling to the triplet alone. In cubic symmetry the LO^Γ phonon involves the A_1 representation of T_d (origin of coordinates taken at a Ga site) In the C_{3v} symmetry deduced for the $(\text{Cu-Li})_{\text{III}}$ center from the ODMR data, the symmetric A_1 representation is compatible with Γ_1 which represents motion along the defect axis.

We conclude from the comparison with band phonons that both local mode of the $(\text{Cu-Li})_{\text{III}}$ complex have the same symmetry, presumably Γ_1 of C_{3v} . The motion is thus longitudinal LO -like and involves the neighbouring atoms as well. Since the selection rules for the band phonons agree with an origin of coordinates at a Ga site, (only this origin gives a symmetric LO^Γ phonon) the neighbouring atoms are phosphorus atoms. We suggest that the two local modes of the $(\text{Cu-Li})_{\text{III}}$ -complex are introduced by a coupled motion of Li and P in a linear defect involving Cu and Li, centered on a Ga site (19). A bond-centered interstitial Li between a P-atom and a Ga-site substituent (presumably Cu_{Ga}) may give rise to such a mixed motion.

Summarising, both local modes may be perturbed LO modes as is reasonable from symmetry arguments. It may be argued that mixing into TO modes in higher order perturbation theory splits the local mode into the two observed modes $1m1$ and $1m2$. This requires that the symmetry remains overall Γ_1 like (LO -like) despite this perturbation. On the other hand, a splitting of a Γ_2 -like local mode into a longitudinal and a transversal mode seems unphysical. Firstly, we do not observe different symmetry for the two modes. Secondly, such modes are generally observed to have widely different energies, with the transverse vibration at lower energy. Thus we do not consider this suggestion as probable.

Conclusions

The $(\text{Cu-Li})_{\text{III}}$ BE center is shown to involve Cu and Li from doping experiments. The involvement of Li is explicitly proved by Li isotope doping which gives a substantial shift of the local phonon mode energies. From mixed isotope doping it is concluded that most probably only one Li atom is present in the defect.

The electronic lines of the BE luminescence are suggested to result from a small splitting of the multivalley degenerate bound electron states. They couple to the more tightly bound holes to form two sets of partly overlapping singlet-triplet BE states. The characteristic singlet-triplet configuration is a generic result of a hole attractive central cell dominating a defect associate. The compressive strain field created locally at such a defect splits the tightly bound hole states with an orbital singlet ground state as a result. Only very few cases of splitting of the electron states have been demonstrated (13).

Usually the electron binding results in an isolated lowest orbital singlet, giving only one pair of S-T states under the above circumstances. The additional splitting of the $(\text{Cu-Li})_{\text{III}}$ BE states indicates a small splitting of the electron states caused by a weak perturbation of the trigonal symmetry deduced from the ODMR measurements. It is suggested that the small magnitude of this perturbation renders it possible for both pairs of singlet-triplet BE states to be observable, in contrast to the cases where a strong axial field of other symmetry than trigonal causes a larger splitting of the electron states, separating one singlet electron state from the rest. The latter case is found for (Cu-Li) centers of lower symmetry, such as the orthorhombic $(\text{Cu-Li})_{\text{I}}$ center (5) and the $(\text{Cu-Li})_{\text{V}}$ center (6). A model for the microscopic identity of

the $(\text{Cu-Li})_{\text{III}}$ defect associate is suggested on basis of the information collected from the doping experiments, the electronic configuration of the BE lines and the local mode structure in the phonon sideband. The overall hole-attractive central cell of the neutral isoelectronic $(\text{Cu-Li})_{\text{III}}$ associate is proposed to be caused by the double acceptor Cu_{Ga} . To ensure charge neutrality a pair of group I interstitial donors is suggested to pair with the Cu_{Ga} substituent. Since the defect is found to be oriented along the $\langle 111 \rangle$ direction the small Li atom is assumed to be bond centred between the Cu_{Ga} and a P host atom. This configuration is proposed to account for the sharp Li related local modes in the $(\text{Cu-Li})_{\text{III}}$ spectrum. Thus we suggest a model for the identity of the $(\text{Cu-Li})_{\text{III}}$ center as a $\langle 111 \rangle$ -oriented $\text{Li}_{\text{Ga}}-\text{Cu}_{\text{Ga}}$ defect associate, of the molecular isoelectronic type.

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References

1. P.J. Dean, J. Luminescence, 7, 51 (1973)

2. E. Cohen and M.D. Sturge, Phys. Rev. B 15, 1039 (1977)

3. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, Phys. Rev. B 25, 7719 (1982)

4. H.P. Gislason, B. Monemar, P.J. Dean, D.C. Herbert, S. Depinna, B.C. Cavenett and N. Killoran, Phys. Rev. B 26, 827 (1982)

5. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, A. Kana'ah and B.C. Cavenett, manuscript submitted to Phys. Rev. B.

6. H.P. Gislason, M.E. Pistol, B. Monemar, A. Kana'ah, B.C. Cavenett, manuscript.

7. P.J. Dean, Phys. Rev. B 4, 2596 (1971)

8. P.J. Dean, Proc. Int. Conf. on Luminescence, Leningrad 1972, Ed. F. Williams (Plenum Press, 1973) p. 538.

9. B.C. Cavenett, Adv. Phys. 30, 475 (1981).

10. J.L. Yarnell, J.L. Warren, R.G. Wenzel and P.J. Dean, Neutron Inelastic Scattering 1, 301 (1968).

11. A. Kana'ah, B.C. Cavenett, H.P. Gislason, M.E. Pistol and B. Monemar, manuscript.

12. J. van W. Morgan and T.N. Morgan, Phys. Rev. B 1, 739 (1970).

13. H.P. Gislason, B. Monemar, P.J. Dean and D.C. Herbert, Physica 117B & 118B, 269 (1983).

14. P.J. Dean, W. Schairer, M. Lorentz and T.N. Morgan, J. Luminescence 9, 343 (1974)

15. T.N. Morgan, Phys. Rev. Lett. 21, 819 (1968).

16. D.J. Robbins and P.J. Dean, Adv. Phys. 27, 499 (1978).

17. P.J. Dean and D.C. Herbert in Topics in Current Physics, Vol. 14, Excitons, Ed. K. Cho (Springer, Berlin 1979) pp 55-182.

18. J.W. Corbett and J.C. Bourgoin in Point Defects in Solids, Vol. 2, Ed. J.H. Crawford Jr. and L.M. Slifkin (Plenum Press, New York 1975) ch 1.

19. The suggested model of a mixed Li-P motion was suggested by T.N. Morgan, which we gratefully acknowledge.

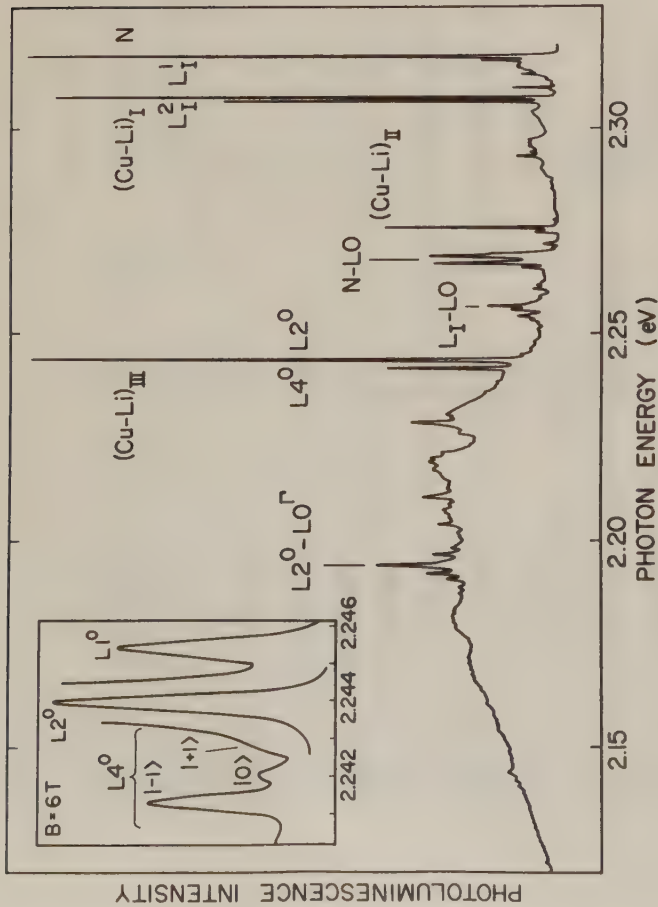


Fig. 1 Low temperature PL spectrum of a typical epitaxial GaP wafer, co-doped with Cu and Li. Three independent Cu-Li centers are seen, (Cu-Li)_{I-III}. The electronic lines L2⁰ at 2.2440 eV and L4⁰ at 2.2419 are observed at 4°K for the (Cu-Li)_{III} bound exciton. As shown in inset, L4⁰ splits into 3 subcomponents in a magnetic field of 6T, while L2⁰ remains unsplit. A third electronic line L1⁰ at 2.2454 eV is also a singlet as shown in the inset.

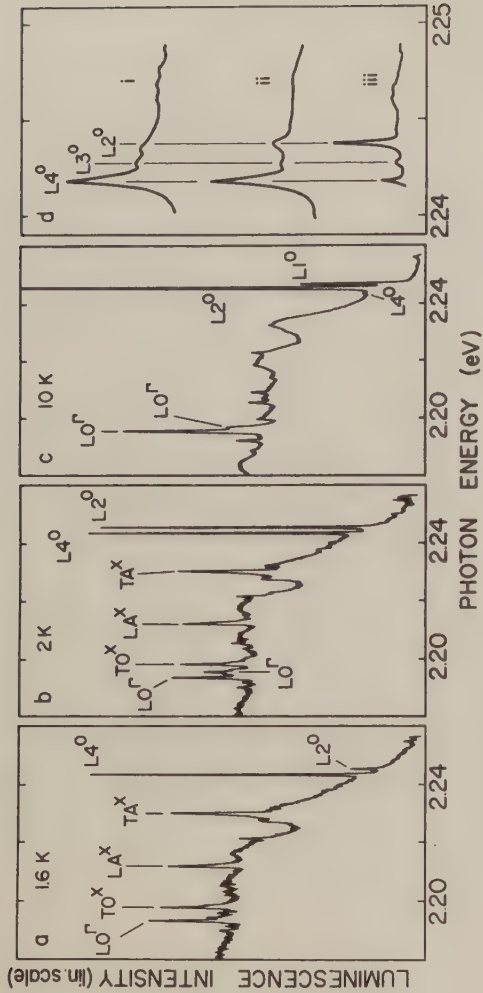


Fig. 2 Low temperature PL spectra of the (Cu-Li)_{III} luminescence.

The magnetic triplet L4⁰ dominates the spectrum at the lowest temperatures in (a). The strong phonon coupling to the X-zone boundary phonons is clearly seen for this line. At slightly higher temperature the singlet L2⁰ grows stronger (b). This line does not couple to the X-zone boundary phonons, but both lines show similar coupling to L0^Γ. At higher temperatures (c) L4⁰ disappears whereas a second singlet L1⁰ appears. Both singlets show a similar phonon coupling. In (d) finally is shown a blow up of the three electronic lines L2⁰-L4⁰ at three different low temperatures (1.6-3K), also showing weakly the second triplet L3⁰.

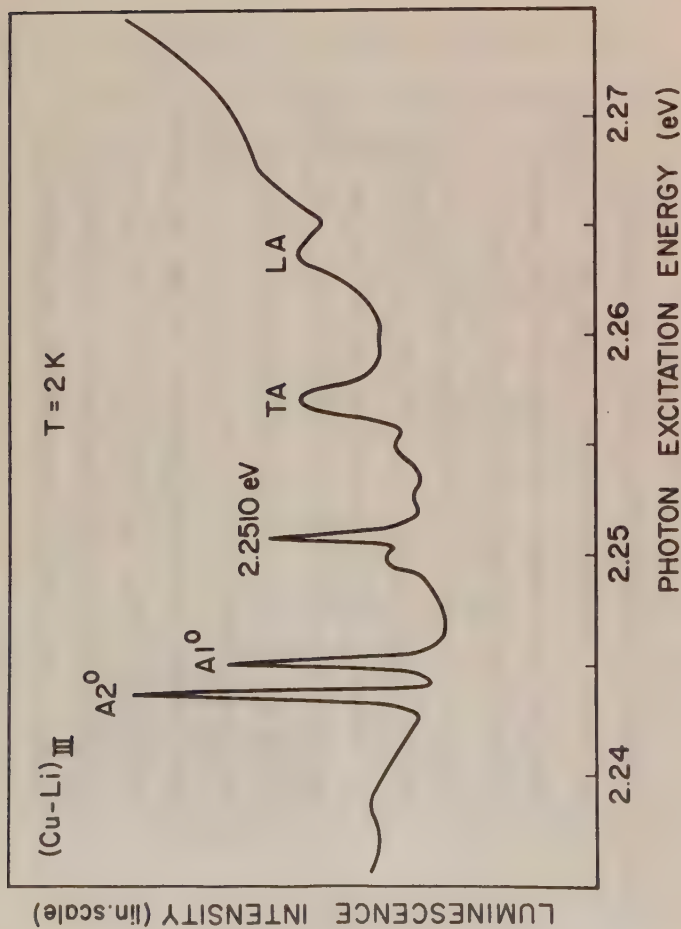


Fig. 5 PLE spectrum of the $(\text{Cu-Li})_{\text{III}}$ luminescence measured with a tunable dye-laser excitation at low temperature. The detection was set to 2.2 eV. The very weak signal is superimposed on a strong background (suppressed in the figure) due to low concentration of the center in the material. Only the two singlets A_2^0 at 2.2440 eV and A_1^0 at 2.2454 eV are observed (L_2^0 and L_1^0 in PL) with comparable strength. No signs of the triplets are detectable. The line at 2.2510 eV is possibly related to the $(\text{Cu-Li})_{\text{III}}$ spectrum.

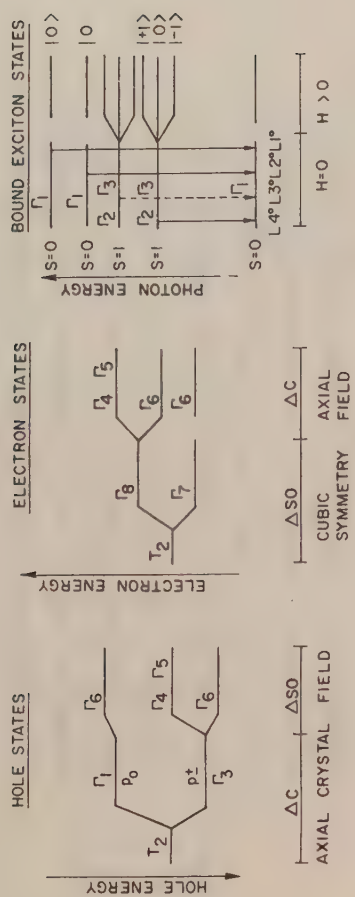


Fig. 6 The figure illustrates the electronic configuration of the $(\text{Cu-Li})_{\text{III}}$ with a schematic level diagram. To the left the hole states are shown with the spin-only like $|0\pm 1/2\rangle$ state as the ground state of the holes. The electron states in the middle are shown to split in a qualitatively similar way. The spin-orbit splitting is assumed to be of similar order of magnitude as the crystal field splitting for the electron. The general hypothesis is that two closely spaced spin states ($\Delta E = 1 \text{ meV}$) result because of the local strain field. Both these states couple to the hole ground state to give the two sets of BE singlet-triplet states shown to the right. The spacing between the two sets is determined by the splitting of the electron states, while the exchange interaction governs the splitting within each set as usual.



Neutral (Cu-Li) complexes in GaP: The (Cu-Li)_v bound exciton at 2.172 eV

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Abstract

A detailed study of a complex defect in GaP created by low temperature Li diffusion into previously Cu-diffused GaP is presented. This (Cu-Li)_v defect is electrically neutral, and binds an exciton with the lowest electronic state at 2.172 eV. The electronic structure of this bound exciton (BE) has a triplet-singlet pair as a lowest energy configuration, with an electron-hole exchange splitting of ≈ 2 meV, while higher excited BE states are observed around 2.26 eV. Such an electronic structure is typical for complex defects in GaP with a hole attractive central cell potential, and in addition experiencing a strong local strain field of compressive sign. Thermal quenching data are consistent with a conventional HTL model where the hole is bound in a localized potential and the electron is bound by Coulomb forces from the hole by a typical donor binding energy of ≈ 80 meV. The simplest model for the identity of the defect, con-

sistent with the body of experimental data presented, has the structure of 3 foreign atoms in a configuration CuGa-Li_i-Cu_i. ODMR data suggest that the Li_i is located off the trigonal CuGa-Cu_i axis, so that the total configuration of the defect is bent in a [110] plane.

I. INTRODUCTION

For some time, there has been considerable interest in the bound exciton spectroscopy of neutral defect complexes in semiconductors. This class of defect is characterized by charge neutrality to the surrounding lattice in the sense that the defect does not bind any electronic particles in its ground state. A typical excited state of such a defect can be described as an exciton bound to the neutral centre, which then contains no other electronic particles than the electron-hole pair. Accordingly, the neutral centres are sometimes referred to as isoelectronic complexes, by analogy with the substitutional isoelectronic defects [1]. This notation is perhaps somewhat misleading and will therefore be avoided below.

The simplest cases of neutral complexes involve pairs of isoelectronic impurities on different sites, such as the NN pairs [2] and perhaps Sb pairs [3] on P sites in GaP. Another type of complex consists of a donor-acceptor pair on nearest neighbour sites, such as the CdGa-Op centre in GaP [4,5]. In this case the complex may be regarded as neutral since the local bonding requirements are fulfilled by the closely associated pair.

Group I species are often found to be fast diffusers as ionized interstitials at elevated temperatures in compound semiconductors [6]. On interstitial sites they are expected to act as single donors, and as such they can form complexes with acceptorlike substituents. Whether such a complex is

neutral or charged should depend on the number and the local arrangement of the acceptorlike and the donorlike parts of the complex. Examples of previously studied neutral complexes are the $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_p$ centre [7] and the $\text{Cu}_{\text{Ga}}\text{-Cu}_i\text{-Cu}_i$ centre in GaP [8].

The electronic configuration of the bound exciton states closely reflects the local symmetry of the defect binding the exciton as well as the overall sign of the short range strain field created by the defect centre. The $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_p$ associate in GaP e.g. gives rise to a local tensional strain, as recognized by the symmetry of the bound hole states. This is also true for the Cd-O complex in GaP [9]. By contrast, several centres involving Cu in GaP [8,10] and InP [11], as well as Li in Si [12] and Cu+Li in GaP [13] have been found to create compressive strain locally at the defect. All of these centres seem to have the common character of a holeattractive central cell, with a localized hole wave function confined to the vicinity of the defect. Consequently the holes experience a large overlap with the local crystal field created by the defect complex. For a compressive sign of the strain field it has been shown that the hole states are orbitally non-degenerate, since an axial strain field increases the binding energy of hole states derived from the spin-like p_0 states, but decreases that of the $p_{\pm}$ states [3].

When an electron and a hole form bound exciton states the electronic configuration of the BE states depends on the magnitude of the exchange interaction between the two parti-

cles. In materials where the electron-hole mass ratio is very small, for example InP and ZnTe, the exchange splitting of the BE states is in general negligible. Already a small magnetic field then completely decouples the electron and hole states, which then split independently of each other at higher fields. This is the case for the exciton bound to the neutral trap InP:Cu [11], as well as for different neutral and acceptorlike complexes of Cu in ZnTe [14]. Other examples in ZnTe illustrate the occasionally observed tight binding of both electronic particles of the bound exciton. One example is found for ZnTe:Ag, where for the 2.349 eV BE state an appreciable exchange interaction is observed, despite the shallow donor electron binding in ZnTe. This behaviour illustrates that the Hopfield-Thomas-Lynch (HTL) model [15] for exciton binding to isoelectronic traps sometimes fails in the case of neutral defect complexes. For a complex formed by the association of acceptorlike and donorlike parts with an associated local strain field, both electronic particles may be bound more deeply than the simplified scheme of the HTL model predicts, even in such materials.

In semiconductors with larger electron-hole mass ratio, such as Si and GaP with indirect bandgaps, the exchange interaction between the electron and hole bound to a neutral complex typically cannot be neglected. The exchange splitting of rather shallow bound exciton states associates with neutral defects is observed to be on the order of 1 meV in these materials. In the above mentioned case of spin-like hole states coupling to spin-only electron states the BE

states produced have a total spin of $S=0$ or $S=1$. In a series of papers we have focussed our attention towards neutral centres binding excitons of this configuration in GaP. Defect complexes of this type include the COL defect in GaP [8] which was proposed to be a $\text{Cu}_{\text{Ga}}\text{-Cu}_{\text{I}}\text{-Cu}_{\text{I}}$ associate, together with another but deeper Cu related centre in GaP, the 1.91 eV centre binding an exciton at 1.91 eV and tentatively assigned to a $(\text{Cu-Ga})\text{GaCu}_{\text{I}}$ split interstitial complex.

In addition to these Cu-related defects a number of neutral associates appear in GaP which is diffused with Li after a previous Cu doping. Not less than five such Cu-Li centres have been observed via their BE spectra in the near bandgap energy region $h\nu > 2.1$ eV, identified in different types of GaP starting in the material. Of these the most prominent ones, labelled $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{III}}$ are described in separate publications, whereas the third significant centre, the $(\text{Cu-Li})_{\text{V}}$ centre is the subject of this publication. Additional (Cu-Li) related bound exciton spectra occur at lower photon energies $h\nu < 2$ eV, but will not be discussed in this paper.

The Cu-Li centres referred to above have widely different binding energies, ranging from 46 meV for the 2.306 eV $(\text{Cu-Li})_{\text{I}}$ centre, through 110 meV for the 2.242 eV $(\text{Cu-Li})_{\text{III}}$ centre, to 180 meV for the deepest one, the 2.172 eV $(\text{Cu-Li})_{\text{V}}$ centre. Despite the different binding energies, the electronic configuration of the BE states of these centres is similar. The lowest-energy component is an

isotropic triplet accompanied by a singlet line, about 1-2 meV higher in energy for all three centres. Clearly the angular momentum of the hole states is quenched for all these Cu-Li centres. In other words, the bound holes must, in all cases, experience a strain-induced splitting that exceeds the effect of the spin-orbit splitting of the valence band hole states. The spin-orbit splitting of the valence band of GaP and its effects on the bound state is in general reduced through the localization at the defect centre.

In this paper, we shall concentrate on the properties of the (Cu-Li)_IV centre, compare its electronic and vibrational properties with the more shallow Cu-Li centres and discuss the identity of the defect binding the exciton. In Section II, we describe the doping procedure which was employed to produce the (Cu-Li)_IV spectrum. An outline of the experimental techniques is also included in Section II. Section III contains a description of the experimental results from photoluminescence (PL), photoluminescence excitation (PLE) and optically detected magnetic resonance (ODMR). The isotropic splitting of the lowest energy component gives no information about the defect symmetry in Zeeman measurements. The ODMR measurements, on the other hand, give strong signals which clearly reveal a complicated anisotropy pattern. The ODMR data are discussed in a separate subsection, Section III D.

A detailed study of the local phonon modes in the (Cu-Li)_IV system illustrates that the similarities between the three Cu-Li spectra are not limited to the electronic structure

alone. In agreement with our findings for the (Cu-Li)_I and (Cu-Li)_{III} centres isotope doping with Li reveals only one Li atom in the (Cu-Li)_IV associate. The isotope doping experiments are discussed in connection with the PL measurements in Section III A.

In the discussion section, Section IV, we discuss the identification problem for neutral centres in compound semiconductors with reference to the Cu and Cu-Li complexes in GaP. A remarkable similarity between the (Cu-Li)_IV centre, discussed here, and the characteristic-orange-luminescence (COL) centre is pointed out. The corresponding excitons have binding energies which differ by only 5 meV, and the spectral shapes of the luminescence bands are much the same. From the differences we conclude, however, that the (Cu-Li)_IV centre is a reconstruction of the COL centre. A possible model would be the replacement of one of the interstitial Cu atoms of the suggested Cu_{Ga}-Cu_I-Cu_I associate by an interstitial Li atom. The accumulated evidence for this model comes from the shape of the PL spectrum and the phonon structure, together with the orientation of the defect as derived from the ODMR data.

II. Experimental

IIA. Sample preparation

In contrast to the other two Cu-Li centres which are most easily produced in epitaxial wafers and solution grown material, the (Cu-Li)v is strongest in LEC bulk material. A necessary prestage for its formation is a previous Cu diffusion of the GaP starting material at high temperatures, typically 950°C for 1 hour, producing the previously mentioned COL defect. After the Cu diffusion, the samples were rapidly cooled to room temperature by immersing them directly from the furnace into water. A subsequent Li diffusion was then made in the temperature range 350-800°C. The diffusion time was usually 4 hours for the lower temperatures, decreasing to about 1 hour for the higher ones.

After the Cu diffusion the samples often show the characteristic orange-luminescence spectrum. This luminescence band disappears after the Li diffusion, for all Li-diffusion temperatures higher than 350°C. Instead, the (Cu-Li)III and the (Cu-Li)v spectra appear, with different relative strength depending on the Li-diffusion temperature. The presence of the COL spectrum after the Cu diffusion is a necessary prerequisite for the observation of the (Cu-Li)v spectrum after subsequent Li diffusion. Furthermore, the (Cu-Li)v spectrum was favoured for lower diffusion temperatures and longer diffusion time. So it was found that in bulk samples the (Cu-Li)v luminescence was strongest after diffusion at 400°C for 4 hours. The shallower (Cu-Li)III spectrum was strongest in such samples under the diffusion

conditions 800°C for 40 min. Other Cu-Li spectra are usually weak in bulk material.

The diffusions were performed in sealed evacuated quartz ampoules. For the Cu diffusion a thin layer of Cu was evaporated onto the samples as a Cu-diffusion source. In the Li-diffusion step, a pellet of natural Li metal was placed in the ampoule. Separately, samples were also doped with enriched ^6Li isotope in order to trace isotope effects in the spectra. The natural Li metal (92.6% ^7Li , 7.4% ^6Li) served as the ^7Li isotope.

IIB. Experimental Techniques

Photoluminescence measurements were performed at liquid helium temperatures using the 5145 Å Ar⁺ laser line as an excitation source. A typical excitation intensity was 100 mW. The PL spectra were dispersed through a 0.75 m double grating monochromator (Jarrell Ash) and detected with an S20 extended photo multiplier tube. The signal was recorded with a Nicolet 1170 signal averager. The optically detected magnetic resonance measurements were partly made at Hull in a superconducting magnet system [16] operating at a microwave frequency about 9 GHz. The spectral response of the ODMR signal was analyzed through a Spex 1402 monochromator and an S20 photomultiplier. The luminescence was excited with the 5145 Å argon laser line also in the ODMR measurements. Similar ODMR measurements were also made at Linköping

University employing a modified 9 GHz Bruker ER 200D-SRC system combined with an Oxford ESR 10 cryostat.

Photoluminescence excitation measurements were performed with a tunable-dye laser excitation with narrow band detection through a monochromator or using filters to select a broader part of the PL band. In both cases the signals were very weak.

III. Experimental results

IIIA. Photoluminescence spectra

Figure 1 shows the photoluminescence spectrum of the (Cu-Li)v centre for an LEC bulk sample, Cu and Li doped under the optimal conditions, as described above. The spectrum consists of a pair of electronic lines, a magnetic singlet line L¹⁰ at 2.1742 eV and a triplet line L²⁰ at 2.1721 eV, accompanied by a rather strong sideband towards lower photon energies. The shape of the phonon sideband is overall reminiscent of the Cu-related COL luminescence [8]. For the more shallow Cu-Li spectra the electron phonon interaction decreases with decreased localization, to become characteristic for a dominant coupling to the one phonon density of states of the host in the case of the shallow (Cu-Li)_I exciton.

For the (Cu-Li)v centre the shape of the phonon sideband is typical for the coupling to quasilocalized phonon modes, induced by the defect and enhanced by the localization of

the exciton wave function in the vicinity of its central cell. Modes of this kind are responsible for the broad envelope of phonon replicas building up the phonon sideband, upon which a set of discrete phonon replicas of various origin is superimposed. An important group of low-energy phonon modes gives rise to a partly resolved peak on the high energy edge of the TA density of states phonon wing. These localized modes, which are resonant with the TA branch have phonon frequencies about 6-8 meV. These phonons seem to have closely related counterparts in the COL spectrum, where three well-resolved sharp low-energy modes occur at similar frequencies (5.3, 6.8 and 8.8 meV, respectively). In the COL spectrum these phonon modes were interpreted as the local vibrations of the two interstitial Cu atoms in the plane of the Cu_{ga}-Cu_j-Cu_j associate. It was suggested that such vibrations were characteristic for heavy interstitial species [8,17,18]. We have not encountered low-energy modes of this kind in other Cu-Li spectra in GaP. In ZnTe, on the other hand, localized modes of even lower energy have been observed in the BE spectra of Ag-related neutral complexes and attributed to interstitial Ag vibrations [14]. These common features of the COL and the (Cu-Li)v spectra will be discussed below in view of a possible relation between the defects causing the two spectra.

Another striking similarity between the COL and the (Cu-Li)v spectrum is the absence of the X-zone boundary phonon replicas TA^X, LA^X and TO^X which dominate the coupling to the forbidden triplet transition in the other Cu-Li spectra [20]. The zone-centre LO phonon is present,

is particularly obvious in Figure 2, which shows the (Cu-Li)v spectrum at two different temperatures. At the lower one, thermalization favours the forbidden triplet, which dominates the spectrum together with its phonon replicas. At slightly higher temperature, the singlet state gets thermally populated and the triplet line disappears due to its forbidden nature. We note that there is no difference observable in the phonon coupling of the two components. The broad and strong 27.5 meV replica denoted by LA in Fig. 2 is still another common feature in both spectra. In the COL spectrum its counterpart at 27.1 meV was interpreted as a perturbed LA mode and believed to involve the motion of the Cu₆ substituent [8]. In the COL spectrum this suggestion was supported by the substantial isotope shift of this mode when substituting ⁶³Cu for ⁶⁵Cu. No such shift could be observed in the (Cu-Li)v spectrum, however, presumably because of broader line widths.

The appearance of true local mode replicas in the (Cu-Li)v spectrum clearly distinguishes this spectrum from the COL spectrum, which shows no such modes. These replicas occur beyond the phonon cutoff frequency of the GaP host lattice and are shown in greater detail in Figure 3. The figure illustrates the results of doping with the two Li isotopes ⁶Li and ⁷Li. In view of all the above dissimilarities between the (Cu-Li)v spectrum and the more shallow ones, it is interesting to note that as far as the isotope doping is concerned all Cu-Li spectra are largely identical. Thus the (Cu-Li)v spectrum has two Li-related local modes at

and 61.9 meV for ⁷Li. As obvious from Figure 3, there are other features present in the spectrum in this energy range, but they have been carefully investigated and found to be unrelated to the local modes associated with (Cu-Li)v. In agreement with the results for other (Cu-Li) spectra in our investigation [13,20] mixed isotope doping with approximately equal amounts of both isotopes in the ampoule during diffusion, reveals no new phonon modes.

The results from the isotope doping are most easily interpreted in terms of only one Li atom in the defect complex. Certainly the case of two or more Li atoms in a coupled motion can be excluded. The latter configuration inevitably leads to vibrational modes involving motion of mixed Li isotopes when both isotopes are present in the material. If not detectable from the natural abundancies, equal amounts of both isotopes would then clearly reveal such mixed modes. Instead, only the ⁷Li and the ⁶Li modes appear in the spectrum, with similar strength upon mixed isotope doping. The same was found for the (Cu-Li)_I and the (Cu-Li)_{III} centra. In the former case even the presence of 7.4% ⁶Li in natural Li could be resolved in the local mode spectra, with approximately correct intensity.

IIIB. Temperature quenching of the PL emission

The influence of a rise in temperature on a PL spectrum such as the one in Fig. 1 is two-fold; thermal broadening effects and quenching of the total emission intensity above a cer-

tain temperature. The first effect is most dramatically seen as a broadening of the electronic lines (and consequently any sharp phonon replicas of these lines), due to a rather strong linear coupling to low energy phonons. A detailed analysis of such effects was presented for the COL emission in GaP [18], and a similar thermal broadening and quenching of the electronic lines was observed with the (Cu-Li) γ spectrum as shown in Fig. 4 for a few temperatures. We shall not analyze these phenomena in detail here, however. We note that the quenching of the no-phonon line by phonon-broadening does not affect the total intensity of the entire emission phonon envelope. Therefore the discussion based on total thermal quenching of the emission, which is an electronic effect, is not affected by the details of phonon coupling active in quenching the electronic (no-phonon) lines.

Fig. 5 shows the temperature dependence of the total emission intensity for temperatures up to 75K. At low temperatures the emission intensity is constant, but starts to decrease drastically around 60K to be at an undetectable level above about 75K in our samples. It is possible to analyze the thermal quenching behaviour in terms of a single activation energy E_1 for the non-radiative competing process to the (Cu-Li) γ emission, according to

$$\frac{I(0)}{I(T)} - 1 = I_0 \cdot e^{-E_1/kT}$$

where $I(0)$ and $I(T)$ are the PL intensity at very low temperature (say 2K) and at the actual temperature of measure-

ment, respectively [21]. From Fig. 5 an activation energy of 80 ± 10 meV is deduced from such a procedure. The most plausible interpretation of an activation energy for a non-radiative competing process in this case would be the thermal liberation of one (or both) charge carriers from the defect in the BE state.

For the (Cu-Li) γ BE the total binding energy of the BE is $2.350 - 2.172 \approx 0.178$ eV at low temperatures. This is considerably higher than the observed activation energy of 80 meV, which suggests that we probably do not observe the liberation of the BE as a whole. Rather one of the particles would be assumed to be thermally excited, leaving the other at the defect, which is of course still sufficient to quench the BE emission.

If we assume that the (Cu-Li) γ centre is dominantly hole attractive, due to a Cu_{Ga} central cell component, one would expect the electron to be thermally excited first. Electron (shallow donor) binding energies on Ga-sites in GaP are typically found to be of the here observed order of magnitude (e.g. 82 meV for Si_{Ga}). We shall further relate these observations from thermal quenching to the electronic structure of the 2.172 eV BE below, in the discussion section (IV:A).

IIIC. Excitation spectra

Excitation spectra with tunable dye laser excitation have given crucial information about the electronic structure of neutral defects in GaP, since also the excited electronic states of a BE can be revealed. A good example is the COL 2.1774 eV centre in GaP, where only one electronic state is seen in PL emission, but several in PLE spectra [8]. For the (Cu-Li)_v BE emission, the observation similar PLE spectra was attempted. The intensities in PLE were extremely weak, mainly due to the very low oscillator strength of the BE states for (Cu-Li)_v (similar to the cases of (Cu-Li)_I [13] and (Cu-Li)_{III} [20]). Actually, the lowest energy triplet-singlet pair at 2.172 - 2.174 eV could not be detected above the noise level in our experiment (partly due to an unfavourably low dye efficiency in that region). A higher photon energy, however, stronger electronic transitions are seen in Fig. 6, with resolved peaks at 2.254 eV, 2.260 eV and 2.266 eV, respectively. These features are broadened, probably due to a short lifetime when they efficiently transfer excitation down to the lowest S-T pair of the defect. Such stronger excited states are also seen with the Cu-related COL-defect [8] and the 1.911 defect [10]. They are believed to originate from electronic excited states of the BE, connected to the p_i^1 hole states of the BE in all cases [8,10].

IIID. ODMR spectra

The ODMR results for the (Cu-Li)_v complex will be reported in some detail separately [22], and therefore we only present a brief account of the most important experimental results in this section. ODMR data have been obtained in photoluminescence, i.e. the excited state of the defect, the bound exciton state, is being probed. It is known from Zeeman data that the lowest energy BE state is a triplet state, approximately isotropic in Zeeman spectra. The interpretation of ODMR data is therefore in principle simple, since we have to assume triplet resonances.

A typical ODMR spectrum taken with a microwave frequency of 9.25 GHz is shown in Fig. 7. The spectrum is of unusually strong intensity, typically 5% of the luminescence intensity is modulated by the microwave field in a total intensity detection mode (no polarizers employed). The spectrum contains a strong low field resonance at $\approx 0,13$ T and in addition a large number of components centered around $g \approx 2$. The low field resonance is assumed to be the $\Delta M = 2$ contribution to the spectrum, unusually strong in this case, while the complicated part centered around $g \approx 2$ is referred to the $\Delta M = \pm 1$ triplet resonance contribution. This part of the spectrum is complicated by the fact that another defect spectrum with resonances around $g = 2$ is superimposed. This second spectrum is due to a separate trigonal defect, very efficiently excited via the (Cu-Li)_v defect [22]. By taking ODMR spectra at different microwave modulation frequencies it has been possible to see which components are related to the

(Cu-Li) γ ODMR spectrum, and a complete angular dependence has been taken, as shown in Fig. 8. From a rotation in a (110) plane it seems clear that the defect has very low symmetry, in general 8 components, i.e. 4 inequivalent triplet resonances can be observed in most directions. The $\Delta M = \pm 1$ spectrum is rather close to collapsing when the magnetic field is in a $\langle 100 \rangle$ direction, and the largest splitting is observed close to $\langle 110 \rangle$. The overall orientation of the defect should therefore be close to $\langle 111 \rangle$, but it is probably distorted off a linear configuration, since a $\langle 111 \rangle$ -oriented defect would give a simpler ODMR pattern that is shown in Fig. 8. Since the defect is argued to consist of three atoms, a bent configuration is easily contemplated. A further discussion on the identity of the defects is given below.

A full analysis of the ODMR-spectrum, including an evaluation of parameters in a model Hamiltonian for this centre, is given separately [22].

IV. Discussion

IVA. Electronic structure of the (Cu-Li) γ bound exciton

As demonstrated above, the BE state for (Cu-Li) γ has a magnetic triplet as a lowest energy state at 2.1721 eV, closely followed by a singlet state at 2.1742 eV. No other electronic states are found until around 2.26 eV, i.e. about 70 meV higher up in energy. This situation resembles the picture found for the previously studied COL defect BE in Gap [8], although the splitting between the triplet and sin-

glet was much larger in that case (21 meV compared to 2.1 meV here. Otherwise, as pointed out earlier, the PL spectra for the COL centre and the (Cu-Li) γ centre are very similar; they are close in photon energy and exhibit a very similar phonon coupling (see below).

The model for the formation of a triplet-singlet pair as the lowest energy configuration of a bound exciton has been previously discussed [8], and is well understood in terms of a strong local stress field of compressive sign at the defect. If the effect on bound hole states for this stress field dominates the spinorbit splitting, the lowest hole state is an orbital singlet p_0 state, which means that the corresponding BE states created upon binding also an electron is made up from a combination of a spin-hole and a spin-like electron. The splitting observed between the triplet and singlet state is due to the electron-hole exchange interaction, directly related to the overlap of the corresponding bound particle wave functions at the defect. The triplet state then becomes the lowest energy state in the case of interacting particles of opposite charge.

The electronic structure for the (Cu-Li) γ BE is schematically shown in Fig. 9. The excited strong electronic states in Fig. 6 probably correspond to the doublet configurations derived from the higher $p \pm$ hole states, also appearing strong in the PLE of the COL centre [8]. The low value of the S-T splitting for (Cu-Li) γ should be interpreted as evidence for a small overlap between the electron and hole wave functions, i.e. they are not both strongly localized as

in the case of COL [8] or the 1.911 eV Cu-related defect BE [10]. In fact, the observation of a thermal activation energy of ≈ 80 meV in Fig. 5 is naturally explained as due to the release of a shallow electron to the hole already present at the defect, i.e. we should refer the (Cu-Li)_v BE to the so-called HTL category [15], where one of the charge carriers of a BE (in this case the electron) bound to an "isoelectronic" defect is "hydrogenic" and loosely bound by Coulomb forces. The situation is different with the COL defect, which shows a thermal activation energy for PL quenching of ≈ 170 meV, i.e. the total BE binding energy. This is in turn consistent with the picture of a defect BE with both carriers rather well localized, as also evidenced by the large value of the S-T exchange splitting of 21 meV in that case [8].

From a previous study it is known that interstitial Li gives rise to two shallow donors in GaP, due to occupation of two inequivalent approximately tetrahedral interstitial sites [23]. This is consistent with the shallow binding of the electron in the (Cu-Li)_v BE, although the symmetry of the electron state should be primarily dominated by the electron-repulsive Cu_{ga} site, believed to dominate the localized potential of the defect. This is also under the assumption that Li enters an interstitial site at the defect, replacing a Cu_i in the analogue COL defect (see below).

A difference with the separately studied (Cu-Li)III defect BE is that the lowest energy electronic configuration of (Cu-Li)III is actually two S-T pairs closely intermixed in energy [20]. This is interpreted as evidence for a symmetry very close to trigonal for (Cu-Li)III [20], in contrast to the case of (Cu-Li)_v discussed here, where a quite large distortion from trigonal symmetry is derived from the ODMR data in Fig. 8.

IVB. Vibrational properties from BE spectra

The vibrational structure observed in the phonon sideband of a BE emission contains a considerable amount of information about the local arrangement of the defect, if properly interpreted. Unfortunately the theoretical development of the vibrational structure of a complex defect containing several atoms of both substitutional and interstitial character is not well advanced, and in addition quite complicated. The identity of the defects is seldom well established, which of course is a severe problem in comparison between theory and experiment. Only simple models for substitutional defect complexes have been treated at some depth in the literature [24,25,26].

As was noted previously the phonon coupling of the (Cu-Li)_v defect resembles very much the structure observed for the COL defect [18]. The two spectra are shown in Fig. 10 for easy comparison. The most important difference is the occurrence of two distinct local phonon modes above the

LO^r phonon energy in the sideband of the $(Cu-Li)_v$ BE, which are absent for COL [18]. The broadened low energy modes observed in the COL spectrum [8,18] were found to be related to the motion of Cu interstitials. We believe the quite similar low energy sideband found for the $(Cu-Li)_v$ BE is also primarily due to mixed modes involving the rather heavy interstitial Cu atom believed to remain at the defect from the original COL identity, when the $(Cu-Li)_v$ centre is created (see below). No Cu isotope shifts of these low energy modes could be detected for the $(Cu-Li)_v$ BE, which is explained by the much broader shape of these replicas for $(Cu-Li)_v$ compared to COL.

The true local modes observed in Fig. 3 constitute the direct evidence for the attachment of a Li atom to the complex. The two modes are independent and couple equally strong to both singlet and triplet electronic BE states, which means that they are probably both of A_1 symmetry [27]. The simplest model for the defect, emerging from the analysis of these local modes upon isotope doping, is that only one Cu atom is substituted by Li in the original COL defect, to create the $(Cu-Li)_v$ defect. Why two different local modes are seen, both with A_1 symmetry is not clear, but the bent configuration of the defect discussed below would certainly allow more than one possible such vibration of the defect, involving the Li interstitial. Only one such mode would be expected, if the defect was of the simpler $CuGa - Li_i$ type, in analogue with previous results for the vibrational modes of a defect composed of an interstitial Li and a substitutional acceptor in Si [28]

The total shape of the sideband of the $(Cu-Li)_v$ defect is quite similar in strength to the COL emission, and involves strong contributions from a broad range of lattice phonons in GaP (Fig. 10). The strength of this phonon coupling is understood as derived from the localization of the primary particle of the BE, in this case supposed to be the hole bound to the $CuGa$ central cell of the defect. In fact, the similarity of this broad phonon sideband for the COL BE and the $Cu-Li_v$ BE is strong evidence that $CuGa$ is involved in both defects.

IVC. The possible identity of the $(Cu-Li)_v$ defect

The problem of identification of complex defects in semiconductors is still one of the major unsolved problems in the area, and a bottleneck against stronger interaction between theory and experiment. No unique method is practical to identify complex defects, usually a combination of evidence from different experiments is used to arrive at a plausible conclusion on the identity of the defect. With this background in mind we shall discuss the collection of experimental data displayed in the previous sections for the $(Cu-Li)_v$ defect, and attempt to put forward a plausible model for the identity of the center. It seems natural to divide the discussion into two different parts, on one hand the chemical identity of the impurity atoms involved in the defect and in addition their geometrical positions in the

lattice to form a defect of observed properties.

A starting point in the discussion of chemical identity is that the COL defect is a necessary prestage in the formation of the (Cu-Li)_v defect. The COL defect has recently been studied in considerable detail, and it has been concluded that it is related to Cu only [8]. This means that it is identified as a neutral complex of the nature Cu_{Ga}-Cu_i-Cu_j, i.e. two interstitial Cu atoms are needed to compensate for the double Cu_{Ga} acceptor site to make a neutral complex. More recent investigations with uniaxial stress show that the COL defect has a major axis close to a trigonal direction, which seems to infer that both interstitials preferably will reside on the same side of the Cu_{Ga}. The fact that the COL defect can transform into the (Cu-Li)_v defect at quite low Li-diffusion temperatures is consistent with a high mobility of interstitial Li (and Cu) already at very moderate diffusion temperatures. Since the local mode behaviour on Li isotope doping in this case points towards the participation of one Li atom in the complex, the most natural assumption is that one of the Cu_i interstitials is replaced by a Li_i. This of course does not preclude the reorientation of the defect at the same time, so the Li_i need not occupy a similar interstitial site as does the replaced Cu_i in the COL defect.

Alternative models involving more than one Li atom tend to be more difficult to reconcile with all experimental data.

If two interstitial Li atoms occur in the defect together with Cu_{Ga}, these interstitials must be perfectly isolated vibrationally to not cause any mixed local modes in the mixed isotope doping experiment. This requires that one Li_i atom be placed on a bond on the opposite side of the Cu_{Ga}. Still, this arrangement should give rise to some mode interaction upon mixed isotope doping. A similar argument holds for the possible substitution of Cu_{Ga} by Li_{Ga}. The Li_{Ga} acceptor has not been firmly identified in GaP, but is believed to be deep, associated with some broad IR PL band around 1.2 μm. We believe it is much more difficult to replace a bonded lattice site atom with another species in a low temperature defect reaction, than it is to replace a simple interstitial, which is not bonded. In addition, a Li_{Ga} - Li_i pair as part of the complex should definitely give rise to mixed isotope modes, as shown in the case of the Li_{Ga}-Li_i-O_p defect in GaP [7].

A problem not explained by the previous discussion is the fact that the creation of the (Cu-Li)_v defect was much easier in the bulk material than in LPE epitaxial layers. It is difficult to suggest a simple explanation for this behaviour, without having characterized in detail the residual defects present in both kinds of starting material. Certainly there is no evidence for the participation of atomic species other than Cu and Li in the defect. It seems that the most plausible reason for the dependence on type of starting material would be that the Li diffusion process is influenced by the different background of the residual defects in

bulk and LPE GaP respectively. It could be that other defects attract the Li interstitials more efficiently in LPE material, thereby quenching the formation of the (Cu-Li)_v defect. More detailed work is needed to clarify this question.

Supposing that the (Cu-Li)_v defect most likely consists of a Cu_{Ga} together with one Cu_i and one Li_i, the geometrical arrangement of these atoms needs to be specified to arrive at a complete identification. From the ODMR data it seems likely that the defect is considerably distorted from a <111> orientation. This is also consistent with the observation of just one set of triplet-singlet pair for the lowest energy BE states, in contrast to the nearly trigonal (Cu-Li)_{III} defect where two such sets are seen. A possible configuration of the (Cu-Li)_v defect is shown in Fig. 11. If we assume that the original COL defect, which is a prerequisite of the formation of the (Cu-Li)_v defect, is a (nearly) trigonal Cu_{Ga}-Cu_i-Cu_j configuration (where both the Cu_{Ga} and the two Cu_i atoms may be substantially relaxed along the <111> axis compared to the corresponding ideal high symmetry positions in the GaP lattice), one can imagine that when one Cu_j leaves the defect it may be replaced by another approaching Li_i atom at some secondary axis away from <111>. Such a low symmetry arrangement might give rise to the complicated low symmetry ODMR spectrum observed from the triplet resonances of the BE for (Cu-Li)_v.

V. Summary and Conclusions

A detailed study of a Cu and Li related neutral defect in GaP, created by a sequential diffusion of Cu and Li (in this order) is presented. A strong photoluminescence emission with the lowest electronic line at 2.172 eV is found to be related to this defect, in fact this spectrum is very similar in general shape to the previously studied COL spectrum. It is found that the PL spectrum is associated with a bound exciton recombination at the defect, and the electronic structure has as a lowest configuration a pair of lines, of which the lowest is an isotropic magnetic triplet and the higher one is a singlet, separated from the triplet by a splitting of 2 meV caused by electron-hole exchange interaction in the BE state. Further excited BE states are found around 2.26 eV in dye laser excited excitation spectra for this (Cu-Li)_v defect BE.

This electronic structure with a lowest triplet-singlet pair is rather common for complex defects in GaP (and Si), where interstitials are involved, causing an overall compressive strain field locally at a defect with a predominantly hole attractive central cell potential. It is understood in terms of an effect of the axial strain field on the bound hole states that is larger than the corresponding effect of the spin-orbit splitting. The bound hole is then a P₀ spin-like state, which combines with a similarly spin-like electron state to give a triplet-singlet configuration for the lowest BE states. Thermal quenching data for the PL emission further support the model of a hole attractive central cell

while the electron is bound by about 80 meV in a typical shallow-donor-like state by Coulomb attraction in the conventional HTL model [15].

Several clues to the identity of the defect are given by details in the phonon coupling to the BE, in addition to chemical evidence from the preparation procedure. Low energy quasilocalized phonon modes in the PL spectrum are taken as evidence for the participation of Cu_i in the centre, as also observed for the COL spectrum. Two distinct A₁ symmetry local modes, which are not intermixed upon mixed isotope doping with Li⁶ and Li⁷, provide good evidence that one Li_i interstitial is involved in the defect. The complicated symmetry revealed by ODMR spectra for the defect is evidence for a bent configuration, where a CuGa - Cu_i pair in an approximate <111> direction is supplemented by a Li_i at an interstitial position along a different direction.

VI Acknowledgements

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References

1. P.J. Dean, J. Luminescence **7**, 51 (1973).
2. E. Cohen and M.D. Sturge, Phys. Rev. **B15** (1039) 1977.
3. H.P. Gislason, B. Monemar, P.J. Dean and D.C. Herbert, Physica **117B & 118B**, 269 (1983).
4. T.N. Morgan, B. Welber and R.N. Bhargava, Phys. Rev. **166**, 751 (1968).
5. C.H. Henry, P.J. Dean, and J.D. Cuthbert, Phys. Rev. **166**, 754 (1968).
6. H.C. Casey, Jr., and G.L. Pearson, Diffusion in Semiconductors, in Point Defects in Solids, Vol. 2, ed. J.H. Crawford and L.M. Slifkin, Plenum Press, New York 1975, pp. 163-256.
7. P.J. Dean, Phys. Rev. **B4**, 2596 (1971).
8. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, Phys. Rev. **B25**, 7719 (1982).
9. J. van W. Morgan and T.N. Morgan, Phys. Rev. **B1**, 739 (1970).
10. H.P. Gislason, B. Monemar, P.J. Dean, D.C. Herbert, S. Depinna, B.C. Cavenett and N. Killoran, Phys. Rev. **B26**, 827 (1982).
11. M.S. Skolnick, P.J. Dean, A.D. Pitt, Ch. Uihlein, H. Krath, B. Deveaud and E.J. Foulkes, J. Phys. C. **16**, 1967 (1983).
12. G. Davies, E.C. Lightowers and M.C. do Carmo, J. Phys. C **16**, 5503 (1983).
13. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, A. Kanaah and B.C. Cavenett, submitted Phys. Rev. B.
14. P.O. Holtz, B. Monemar, H.P. Gislason, Ch. Uihlein and P.L. Liu, submitted to Phys. Rev. B.
15. J.J. Hopfield, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).
16. A. Kanaah, B.C. Cavenett, H.P. Gislason, B. Monemar and M.E. Pistol, unpublished.
17. P.J. Dean, B. Monemar, H.P. Gislason and D.C. Herbert, J. Luminescence **24/25**, 401 (1981).

18. H.P. Gislason, B. Monemar, P.O. Holtz, P.J. Dean and D.C. Herbert, *J. Phys.* **C15**, 5467 (1982).
19. P.O. Holtz, B. Monemar, H.P. Gislason, N. Magnea, Ch. Uihlein and P.L. Lin, submitted to *Phys. Rev. B*.
20. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, A. Kanaah and B.C. Cavenett, submitted to *Phys. Rev. B*.
21. M.D. Sturge, E. Cohen and K.F. Rodgers, *Phys. Rev.* **B15**, 3169 (1977).
22. M. Godlewski, W.M. Chen, B. Monemar, M.E. Pistol and H.P. Gislason, unpublished.
23. P.J. Dean, *Proc. Int. Conf. on Luminescence Leningrad 1972*, ed. F. Williams, Plenum Press 1973, p. 538.
24. D.N. Talwar, M. Vandevyver and M. Zigone, *J. Phys.* **C13**, 3775 (1980).
25. R.M. Feenstra, R.J. Hauenstein and T.C. McGill, *Phys. Rev.* **B28**, 5793 (1983).
26. R.J. Hauenstein, T.C. McGill and R.M. Feenstra, *Phys. Rev.* **B29**, 1858 (1984).
27. M.E. Pistol and B. Monemar, unpublished.
28. R.C. Newman, *Infrared Studies of Crystal Defects* (Taylor and Francis, London, 1973).

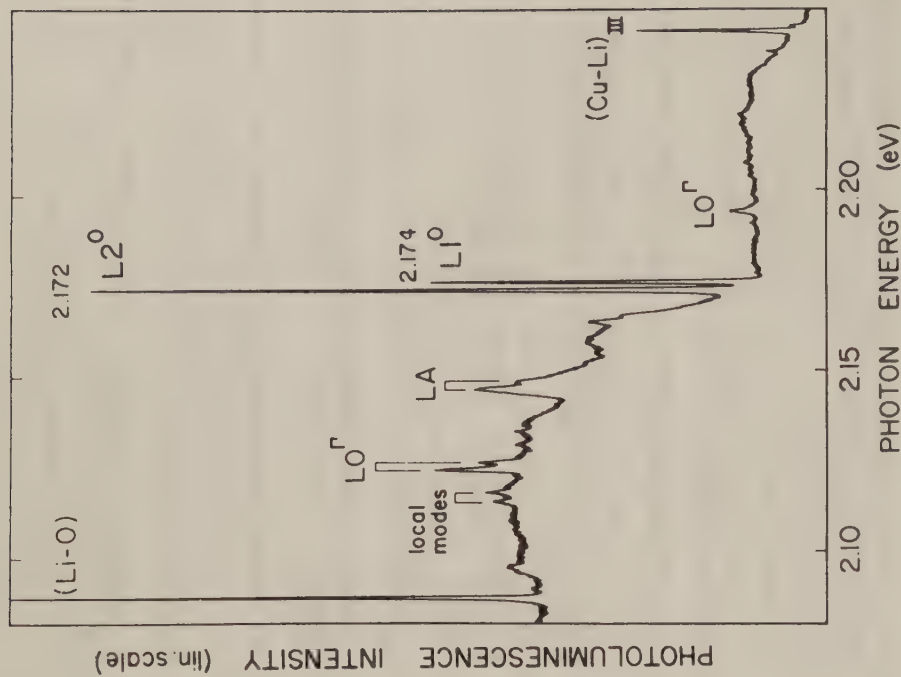


Figure 1 Photoluminescence spectrum of the (Cu-Li)^v bound excitation. Two no-phonon lines are seen L2⁰, a magnetic triplet and L1⁰ magnetic singlet. Also seen are local modes and LO^r and LA bulks phonon replicas. Two other complex defects Li-O and (Cu-Li)_{III} are also present.

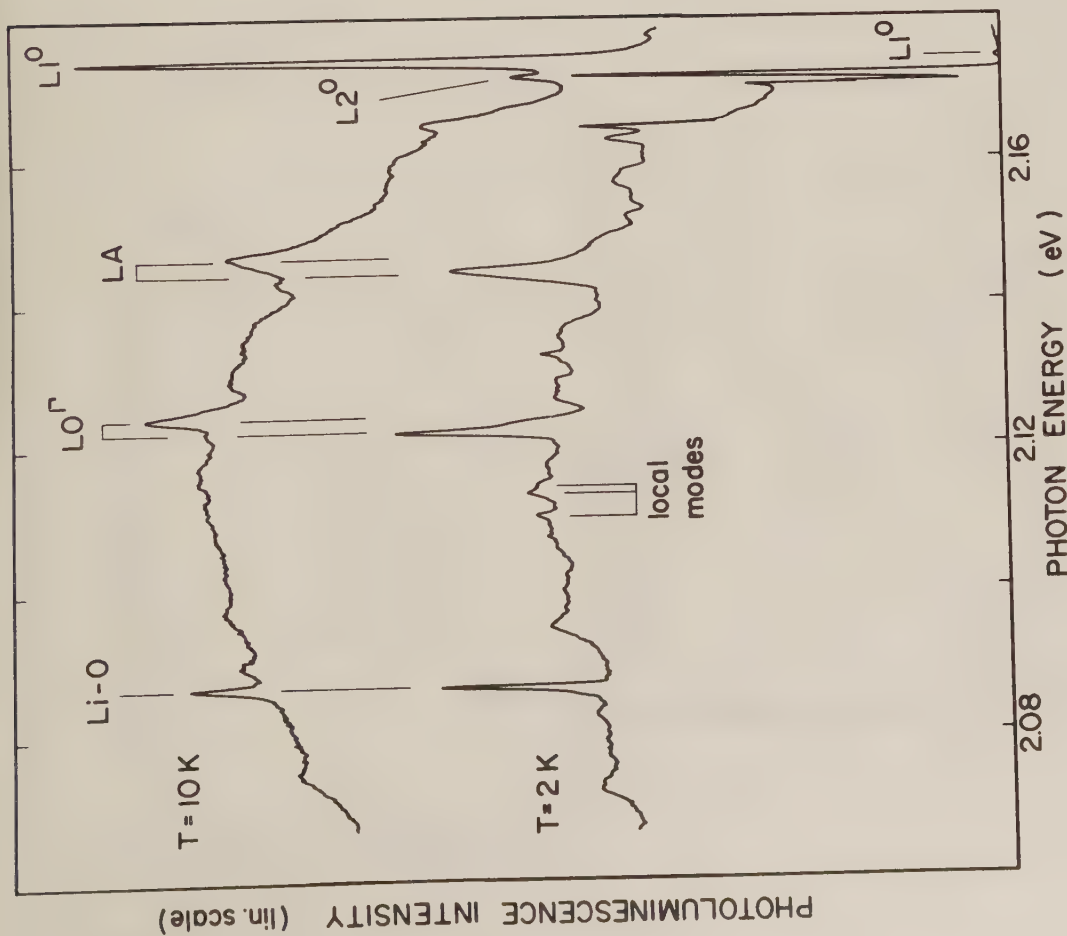


Figure 2 The (Cu-Li)_y bound exciton emission at two different temperatures. The singlet Li^o is seen to dominate at T = 10 K. High temperature also makes the phonon-band broader and more feature less.

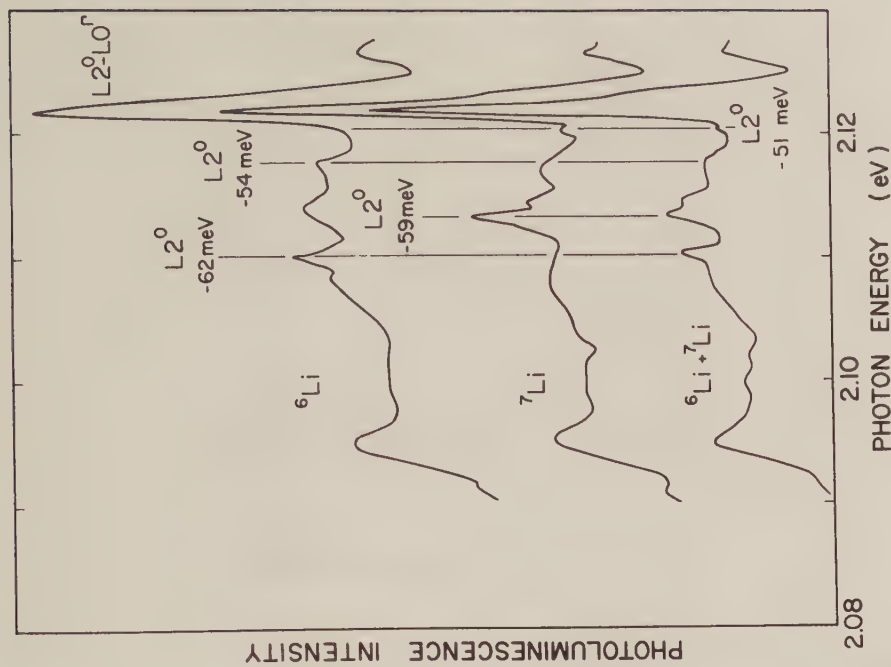


Figure 3 A close view of the local modes. The two modes with energy 51 meV and 59 meV are ⁷Li related. When ⁶Li is diffused they move to 54 meV and 62 meV respectively. With approximately equal amounts of ⁷Li and ⁶Li no new local modes appear. Other features present correspond in energy to sums of other vibrational modes.

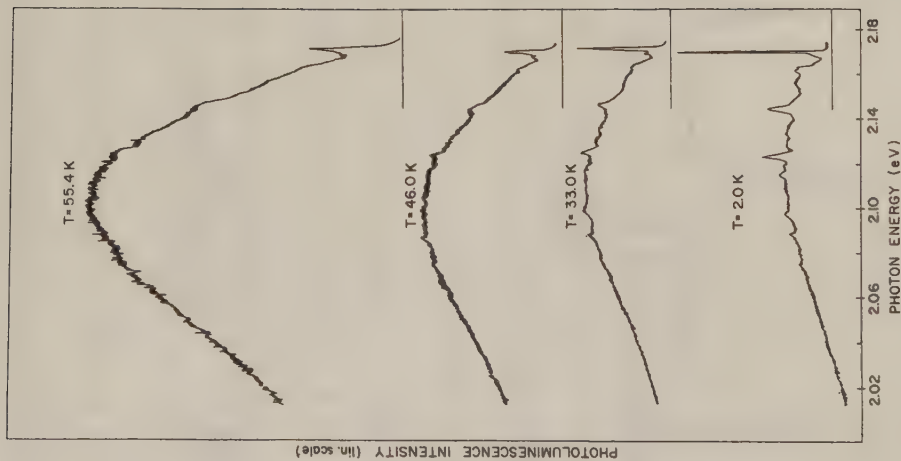


Figure 4 Photoluminescence spectra of the (Cu-Li)₇ bound exciton at different temperatures.

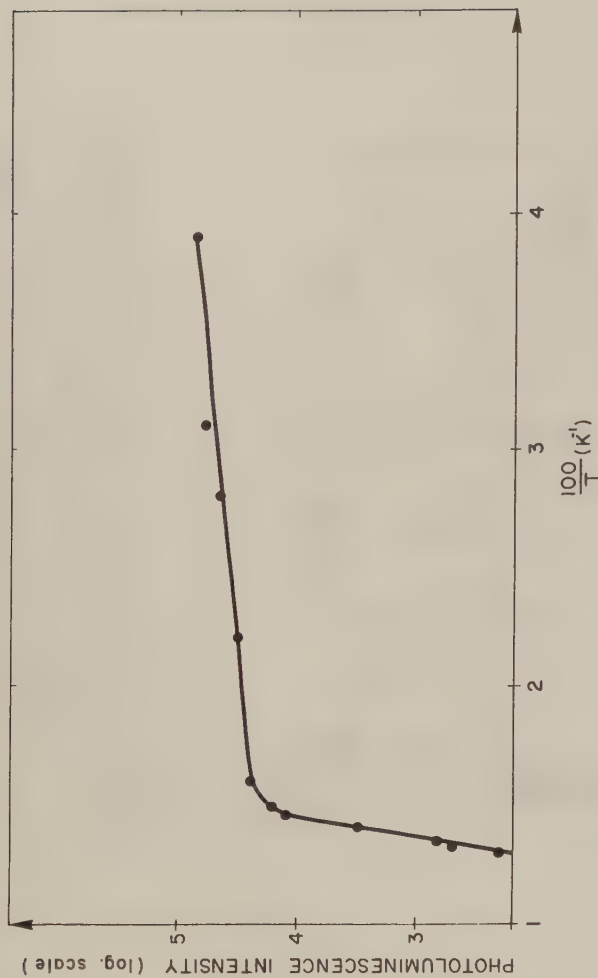


Figure 5 Photoluminescence intensity of the (Cu-Li)₇ BE emission plotted against $1/T$.

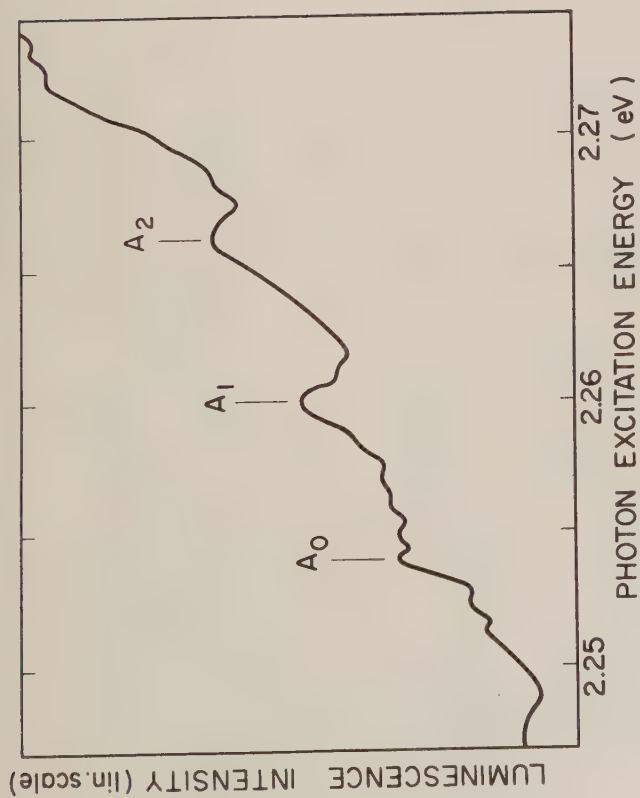


Figure 6 Photoluminescence excitation spectrum. The peaks labeled A₀, A₁ and A₂ are the only peaks consistently obtained. No detailed information is revealed due to the weakness and lifetime broadening of the peaks.

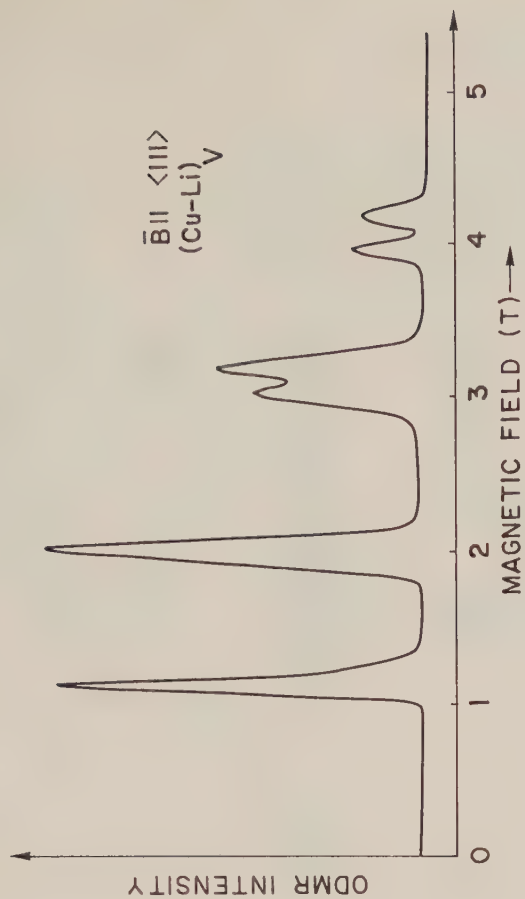


Figure 7 A typical example of the well structured and strong ODMR spectra obtained from the (Cu-Li)_V centre.

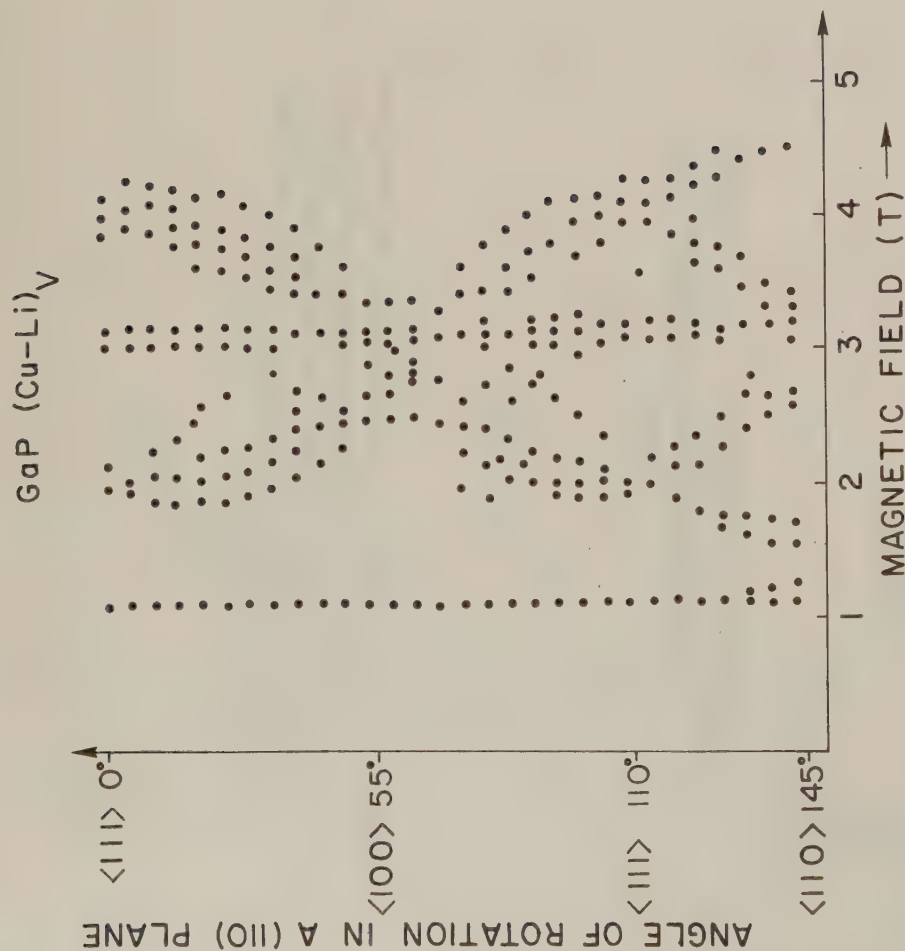


Figure 8 A plot of the complicated angular dependence of the ODMR signal. The spectrum is close to collapsing to with the magnetic field in the $\langle 100 \rangle$ direction. The maximum separation is at the $\langle 110 \rangle$ direction.

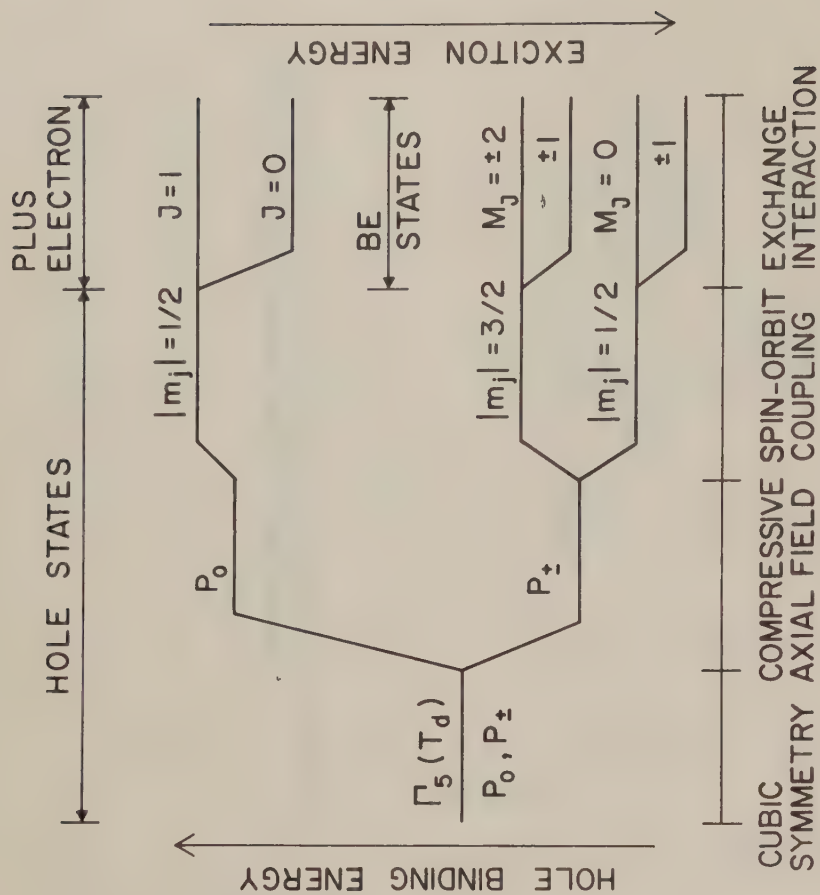


Figure 9 A level scheme of the hole and exciton states for the $(\text{Cu-Li})_V$ bound exciton. The axial stress-field is larger than the hole spin-orbit interaction, giving a spin-only hole state, (p_0 or Γ_6'), as the lowest energy hole state. This hole state couples with a Γ_6 electron giving a singlet ($J=0$) and a triplet ($J=1$) exciton state.

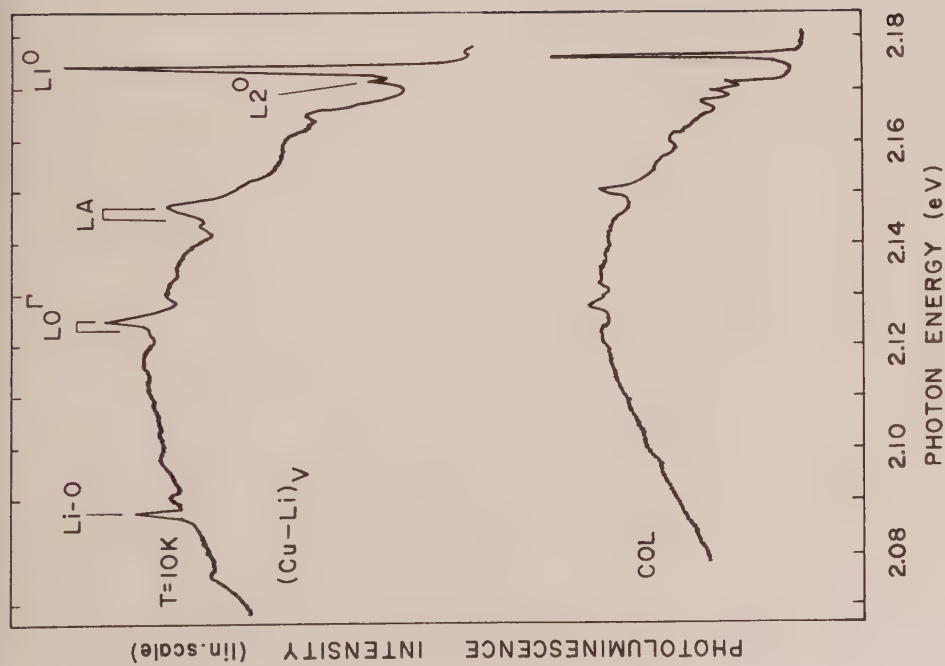


Figure 10 A comparison of the (Cu-Li)_v and COL. The spectra are very similar, differing mainly in the phonon coupling to low-energy (6-8 meV) phonon modes. The COL bound exciton has a large exchange splitting so only the triplet is seen.

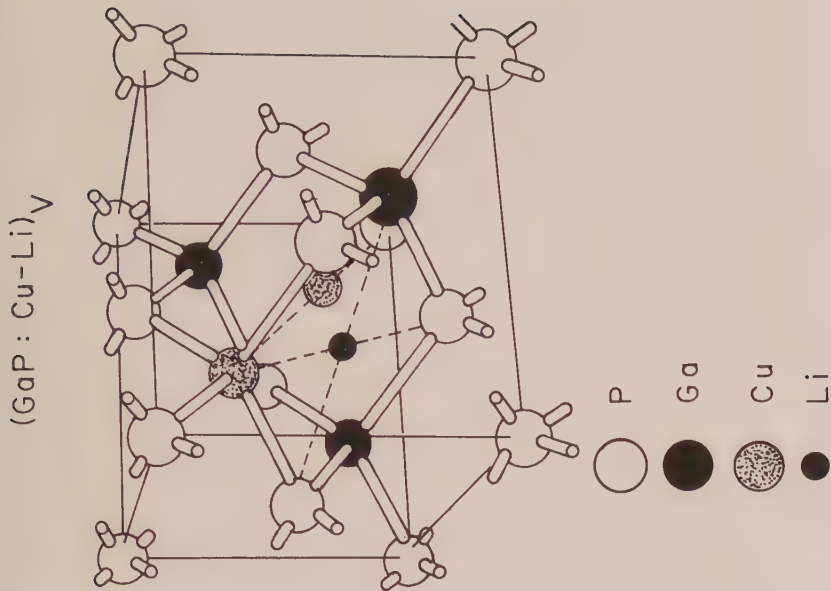


Figure 11 An illustration of the proposed geometrical of the (Cu-Li)_v centre. The Li_i is distorted away from the <111> direction but the main symmetry is axial.

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Abstract

A broad photoluminescence (PL) band peaking at ≈ 1.70 eV in Li-doped GaP is investigated by optical spectroscopy. No electronic lines are observed for this PL spectrum, indicating a strong phonon coupling with a no-phonon energy of ≈ 1.80 eV. ODMR data reveals a triplet configuration for the lowest electronic state of the corresponding defect, which proves that it is a neutral complex defect, binding an exciton in a predominantly hole-attractive local potential with an overall compressive local strain field at the defect. The ODMR data can be

fitted to a standard triplet spin hamiltonian

$$H = \mu_B \cdot \vec{B} \cdot \vec{g} \cdot \vec{S} + D(S_z^2 - 1/3 S(S+1)) + E(S_x^2 - S_y^2)$$

with evaluated parameters $g_x=2.0$, $g_y=1.9$, $g_z=2.05$

$D=1.2 \cdot 10^{-5}$ eV and $E=8 \cdot 10^{-7}$ eV ($x=[001]$, $y=[\bar{1}10]$, $z=[110]$).

The defect therefore has a bent symmetry, and the identity is suggested to involve Li_{Ca} together with two interstitials in a $[110]$ plane, probably both Li atoms.

I. INTRODUCTION

Li is a rapid interstitial diffuser in GaP, and is known to introduce two different interstitial shallow donors in GaP [1]. LiGa is believed to be a deep acceptor, since it has not been observed in optical spectra in the visible spectral region [2]. Neutral "isoelectronic" complexes involving both Li and Cu have been studied recently, and several bound exciton spectra related to such defects are found in the visible region [2-5]. These complex defects are believed to involve CuGa, i.e. Li is incorporated at interstitial sites: [2-4]. LiGa is tentatively believed to be involved, in a complex defect causing a deeper bound exciton emission in the IR around 1.2 eV in GaP [6]. In addition LiGa has been shown to be part of the Li-LiGa-Op complex defect in GaP, giving rise to a bound exciton emission at 2.09 eV in GaP [7].

GaP intentionally doped with Li alone shows bound exciton (BE) spectra and donor-acceptor (DA)-pair spectra associated with the shallow interstitial donors [1], and in addition usually the red Li-Li-O BE spectrum with no-phonon lines close to 2.09 eV [7]. At lower photon energies a broad emission peaking at 1.70 eV is consistently observed with Li doping, as already noted in the earlier work by Dean [7]. In this work a more detailed study of this emission is presented. It is shown to be related to a neutral Li-related complex of low symmetry.

The main body of new information presented in this paper is derived from optical detection of magnetic resonance (ODMR), performed in the emission mode, i.e. the excited state of the

defect is being probed in photoluminescence [8]. ODMR spectra have previously been observed for (Cu-Li) related complex defects in GaP, due to the fact that the bound excitons associated to these defects have a magnetic triplet as lowest electronic state [9,10]. The Li-Li-O defect has two magnetic doublets as lowest electronic configuration [7], which means that ODMR resonances are not expected to be observed, in agreement with experimental findings in this work. The deep red Li-related emission, however, does show an ODMR spectrum typical for a triplet resonance. Such a triplet configuration is possible only if the defect experiences an average local strain field of compressive sign [2, 11-13]. Further the angular dependence of the ODMR resonances clearly show that the defect is bent in a [110] plane.

In Sec II below details about sample preparation and the experimental procedure are briefly summarized. Sec III contains the photoluminescence spectral data, in the absence of microwave resonance and magnetic fields. The broad 1.70 eV band shows no structure from electronic lines, unfortunately. Sec IV gives a description of the ODMR data obtained for the 1.70 eV PL emission band, as summarized above. Finally a discussion of the results on Li-related complex defects in GaP deduced from this work is provided in Sec V. A structural model for the possible identity of the defect causing the 1.70 eV emission band is also suggested.

II. Samples and Experimental Techniques

The samples used for the specific work on Li-doped GaP reported here were small solution-grown platelets, which were selected to be single crystalline. The samples were originally nominally undoped, but contained residual impurities such as S, Si, N and O. Li-doping was performed by diffusion in evacuated quartz ampoules. Li metal pellets were placed on an additional quartz support plate inside the ampoule to avoid serious chemical attack on the ampoule quartz wall during heat treatment. Typical Li diffusion conditions were 600 - 800°C for 1 hour. The ampoules were rapidly quenched to room temperature in water after the diffusion.

Photoluminescence spectra were measured with above bandgap excitation with an Ar⁺ laser, and extrinsic excitation either with a Coherent 590 tunable dye laser system or with a Kr⁺ laser. The spectral dependence was recorded with an S20 photomultiplier via a SPEX 0.85 m double monochromator. ODMR data were obtained with a 9 GHz cylindrical microwave cavity, mounted on an Oxford SR10 He cryostat. The spectral dependence of the ODMR luminescence signal was monitored via a small Jobin Yvon 0.25 m single monochromator. Spectral averaging and storage was performed with a Nicolet 1172 signal averager for both PL and ODMR spectra.

III. Photoluminescence Spectra

In fig. 1 is shown photoluminescence spectrum at 2K for a typical Li-doped solutiongrown GaP crystal used in this study. The entire visible region is shown in fig. 1, and it is obvious

that in this case the 2.08 eV Li-Li-O BE emission completely dominates the spectrum, due to the presence of O in the starting material prior to Li diffusion. Li-related spectra are also seen closer to the bandgap. In the case shown in fig. 1 these spectra are actually dominantly related to various (Cu-Li)-related defects as reported in a separate study [2-3]. This is due to a slight Cu-contamination of the crystal during Li diffusion. In fig. 2 the less prominent spectral regions in fig. 1 are displayed in more detail. The (Cu-Li)_I complex in fig. 2a is responsible for the BE line at 2.306 eV [2]. The deep red broad band finally is shown more clearly in fig. 2b. It has a shape that varies slightly from sample to sample and with different excitation conditions, indicating that it overlaps somewhat with other similarly broad emission bands in the background.

The broad band peaking at 1.70 eV is to be interpreted as an envelope of an emission composed of a weak (not resolved) electronic line (or lines) with a strong phonon coupling. The half-width of the band is about 100 meV, indicating a Franck-Condon shift $[\lambda_i \hbar \omega_i]$ of a similar order [14]. (Here $\hbar \omega_i$ denote the different phonon energies participating in the phonon coupling to the optical transition, λ_i the corresponding coupling strength [15]). The electronic no-phonon line should be around 1.80 eV, judging from the spectral shape in fig. 2b.

IV. ODMR spectra

The recording of ODMR spectra for complex defects in GaP is not very straightforward, because transfer of excitation may easily

occur between different defects. This gives rise to the possibility of registration of ODMR signals from a certain PL spectrum, while the resonance is actually taking place in another higher energy excitation, subsequently transferred to the defect causing the detected emission. [16,17]. In the present case severe Cu contamination had to be avoided, since several (Cu-Li) related defect BE:s give rather strong triplet ODMR signals, [9,10], which may be detected also at lower photon energies due to BE transfer [16]. This is particularly serious for the (Cu-Li)_y BE at 2.172 eV, which gives an unusually strong ODMR signal [4,10]. The 2.09 eV Li-Li-O-related BE emission does not give rise to a detectable ODMR signal. This is understandable, since in this case the lowest electronic lines are magnetic doublets, $M_z = \pm 2$ and $M_z = \pm 1$ respectively [7]. Microwave induced transitions $M_z = \pm 4$ and $M_z = \pm 2$ are forbidden, and in addition there is no strong difference in oscillator strength between the transitions from $M_z = +2, 1$ and $M_z = -2, -1$ respectively down to the BE ground state. Therefore no ODMR effects is expected, nor is it observed for the Li-Li-O PL spectrum.

The broad 1.70 eV band, however, does show a rather weak ODMR signal, as shown in fig. 3. The spectrum is characteristic of a triplet resonance exhibiting pairs of $\Delta M = \pm 1$ lines centered around $g \approx 2$ (i.e. ≈ 3300 G). In addition a strong low energy line is observed at about 1500 G interpreted as due to a $\Delta M = 2$ resonance. The resonance lines are fairly broad, with a half width of typically 300 G, possibly due to an unresolved hyperfine interaction for Li atoms with nuclear spins $I = 3/2$.

The angular dependence of the spectrum was also investigated,

as shown in fig. 4. The defect is found to be bent in a $[110]$ -plane from the clear symmetry pattern observed for the $\Delta M = \pm 1$ lines in fig. 4. A fitting of the angular dependence of fig. 4 was performed with the standard Hamiltonian [8]

$$H = \mu_B \cdot \vec{B} \cdot \vec{g} \cdot \vec{S} + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2),$$

A best fit is obtained with the following parameters

$$g_x = 2.0$$

$$g_y = 1.9$$

$$g_z = 2.05$$

$$D = 1.2 \cdot 10^{-5} \text{ eV}$$

$$E = 8 \cdot 10^{-7} \text{ eV},$$

where $x = [001]$ $y = [\bar{1}\bar{1}0]$ and $z = [110]$

To ascertain the origin of the ODMR signal the spectral dependence of PL was obtained at resonance with a magnetic field of 2900 G, as shown in fig. 5. The spectrum is very similar to the one shown in fig. 2b, indicating that the 1.70 eV band does produce the ODMR resonance. The ODMR-PL band in fig. 5 peaks at slightly higher photon energy than the band in fig. 2b, which can be explained if a lower energy band is in fact overlapping in the PL spectrum of fig. 2b. The problem of excitation transfer from higher energy bound exciton states may be excluded in this case, since the (Cu-Li)-related spectra, being the only realistic candidates for such transfer, give ODMR spectra which are well known from previous work [9,10], and which are easily distinguishable from the spectra found here (figs. 3 and 4).

Consequently it is reasonable to assume as a result of the ODMR data, that the 1.70 eV spectrum is connected with a defect which has a bent configuration in a [110]-plane, and with a lowest electronic bound exciton excitation of a triplet ($S=1$) nature.

V. DISCUSSION

V1. Electronic structure of excitons localized at complex defects

The 1.70 eV broad PL band studied in this work is associated with a complex neutral defect, as evident from the triplet structure observed for the electronic bound exciton state from ODMR data. This is a nice demonstration of the power of ODMR, in a case where the electronic line is too weak to be observed and consequently unavailable for Zeeman spectroscopy. The conditions for observation of a triplet state at lowest energy for a bound exciton has been discussed in previous papers [2-4, 11-13], and will just be summarized here. A triplet state occurs when a spin-like hole is combined with a spin-like electron state, to form a $S=1$ state for parallel spins. In addition a $S=0$ state is present for antiparallel spins higher in energy, split off from the lowest $S=1$ state by the electron-hole exchange interaction energy Δ_{JJ}^{eh} . This situation requires that only two particles (one electron and one hole) are present in the excited state (the bound exciton state), i.e. the center is a neutral one. The condition for obtaining a

spinlike (P_z) hole state is an overall strong compressive stress field at the defect of axial or lower symmetry, which will push down the p_z hole states [11] down in the valence band, by an amount larger than the effect of spin-orbit interaction on the bound hole states. This situation is summarized in fig. 6a. As a contrast is shown in fig. 6b the expected electronic structure for the case of a tensional axial strain field, as for the Li-Li-O defect studied earlier. (The scheme suggested in fig. 6b is simpler than the one suggested by Dean [7], and also in better agreement with experimental data in ref. 7.)

The observation of a triplet bound exciton state thus provides the valuable information that the defect responsible for the 1.70 eV emission is a neutral complex defect with a hole attractive potential in a strongly compressive average local stress field. The low symmetry deduced from the detailed fitting of fig. 4 deviates somewhat from a simple trigonal configuration, and is most conveniently described as orthorhombic. The observation of a strong " $\Delta M=2$ " resonance in the ODMR spectrum is also an indication of a symmetry lower than trigonal. Earlier data on Cu-related [12] and (Cu-Li)-related defects [5, 6, 9, 10] indicate that strong $\Delta M=2$ ODMR lines are seen when the symmetry is drastically different from trigonal, as e.g. in ref. 6 and 10. The three substates of the triplet in a magnetic field are in first order split into the $|0\rangle$ and $|\pm 1\rangle$ states. However the terms $D(S_z^2 - \frac{1}{3} S(S+1))$ and $E(S_x^2 - S_y^2)$ in the triplet spin Hamiltonian, arising mainly from the anisotropic part of the electron-hole exchange interaction, will drastically change the

character of these substates. This is particularly true at low magnetic fields as appropriate for a 9GHz ODMR experiment, where the character of the wavefunctions for these " $|0\rangle$ " and " $|\pm 1\rangle$ " states may have been changed to an extent that m_z is no longer a good quantum number. In that case it is not surprising that the so called " $\Delta M=2$ " transitions in the ODMR spectrum appears as an allowed microwave transition, particularly for defects with symmetry lower than trigonal, in which case the $E(S_x^2 - S_y^2)$ term will have a strong influence on the character of the substates at low fields.

V2. Possible identity of the defect responsible for the 1.70 eV PL emission

The 1.70 eV emission is only observed when GaP is doped with Li, which means that it can be safely stated that Li is part of the defect. The presence of Cu in the defect cannot be definitely excluded since Cu is very easily introduced as a contaminant in GaP during Li diffusion. We have not found any evidence for an enhanced intensity of the 1.70 eV emission with Cu doping, but this is no definite argument against Cu being part of the complex. We have observed that in GaP crystals deliberately doped with both Cu and Li, the 1.70 eV PL band does not appear strongly. Cu-doping alone gives rise to a broad band at slightly lower photon energies, centered at about 1.65 - 1.7 eV [18]. This band is believed to be related to the 0.51 eV Cu-related acceptor in GaP [18, 19], and a separate study reveals that it does not give rise to any ODMR spectrum in the range of magnetic fields employed in this study. This

Cu-related emission could form part of the low energy background in the PL spectrum in fig. 2b, however. No correlation with another dopant is found and the 1.70 eV emission can be found with comparable intensity for Li-diffusion into both doped (n or p) and nominally undoped (doping level $10^{15}-10^{16} \text{ cm}^{-3}$) GaP.

The collected evidence from the photoluminescence spectra in relation to doping and diffusion conditions mentioned above seems to favour a model where LiGa is the dominating hole-attractive central cell of the defect. LiGa is supposed to be a deep double acceptor in GaP, in fact it has not yet been positively identified. It has been argued that the deep (Cu-Li) complexes giving PL emissions around 1.1eV in GaP are in fact deep due to LiGa being part of these defects. On the other hand the Li-Li-O defect is more shallow, with a hole binding energy of only about 200 meV [7]. The partition between electron and hole binding energies for the 1.70eV bound exciton is not known, (temperature quenching data were unreliable, due to spectral overlap with other broad emission bands), but it may be assumed that the hole binding energy is about 500 meV, and the electron binding energy much smaller, say of the order 50 meV. This is natural if the defect is dominantly hole-attractive, in which case the electron is bound as a secondary particle with a binding energy possibly reduced even below the value for a shallow donor electron by the electron-repulsive defect potential dominated by LiGa.

LiGa is a double acceptor, which means that two donor electrons are necessary to make the center neutral and satisfy the

local bonding in a tetrahedral configuration. If no P-site impurities are involved in the defect (which is natural from the above discussion), these donorlike species must be interstitials. Li_i interstitials on the two tetrahedral sites are shallow single donors [1], and two such interstitials would suffice to make a neutral center together with LiGa. Such a model is illustrated in fig. 7, where one interstitial is supposed to occupy a tetrahedral site on a trigonal axis, while the second interstitial is occupying another site off this trigonal direction, so that the total defect configuration is bent. Such a model seems to be in agreement with the symmetry derived above from the angular dependence of ODMR data. As mentioned above it cannot be definitely excluded that one of the interstitials could be a Cu atom. The most likely conclusion, however, is that both interstitial atoms are Li, which means that the defect should be denoted Li_i-LiGa-Li_i.

References

1. P.J. Dean, Proc. Int. Conf. on Luminescence, Leningrad, 1982, Ed. F. Williams (Plenum Press, 1973) p. 538.
2. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean; D.C. Herbert, A. Kanáah and B.C. Cavenett, Phys. Rev. B, March 15, 1985.
3. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, S. Depinna, A. Kanáah and B.C. Cavenett, submitted Phys. Rev. B.
4. H.P. Gislason, M.E. Pistol, B. Monemar, A. Kanáah and B.C. Cavenett, submitted Phys. Rev. B.
5. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, B.D. Cavenett and A. Kanáah, Proc XVII:th Int. Conf. on the Physics of Semiconductors, San Francisco, 1984.
6. A. Kanáah, B.C. Cavenett, H.P. Gislason and B. Monemar, manuscript 1985.
7. P.J. Dean, Phys. Rev. B **4** 2596 (1971).
8. B.C. Cavenett, Adv. Phys. **30**, 475 (1981).
9. A. Kanáah, B.C. Cavenett, H.P. Gislason, B. Monemar and M.E. Pistol, manuscript (1985).

9. A. Kanda, B.C. Cavenett, H.P. Gislason, B. Monemar and M.E. Pistol, manuscript (1985).
10. A. Kanda, B.C. Cavenett, H.P. Gislason, B. Monemar and M.E. Pistol, manuscript (1985).
11. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, Phys. Rev. **B25**, 7719 (1982).
12. H.P. Gislason, B. Monemar, P.J. Dean, D.C. Herbert, S. Depinna, B.C. Cavenett and N. Killoran, Phys. Rev. **B26**, 827 (1982).
13. H.P. Gislason, B. Monemar, P.J. Dean and D.C. Herbert. Proc. 16th Intern. conf. on the Physics of Semicond., Montpellier 1982. Physica **117B**, 269 (1983).
14. T.H. Keil, Phys. Rev. **140** A601 (1965).
15. H.P. Gislason, B. Monemar, P.O. Holtz, P.J. Dean and D.C. Herbert, J. Phys. **C15**, 5467 (1982).
16. M. Godlewski, B. Monemar, W.M. Chen, M.E. Pistol and H.P. Gislason, manuscript 1985.
17. M.E. Pistol and B. Monemar, J. Phys. **C17**, L943 (1984).
18. B. Monemar, J. Luminescence **5**, 472 (1972).
19. H.G. Grimmeiss and B. Monemar, Phys. Stat. Sol (a) **19**, 505

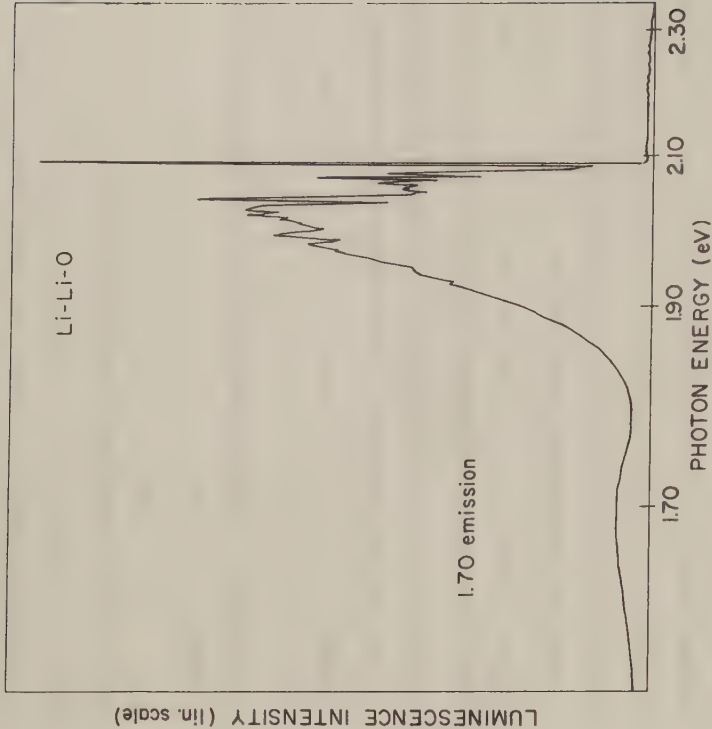


Fig 1. A photoluminescence spectrum at 2K for a Li-doped crystal showing a dominating Li-Li-O bound exciton emission and a band peaking at about 1.70 eV. The luminescence close to the bandgap is weak in comparison.

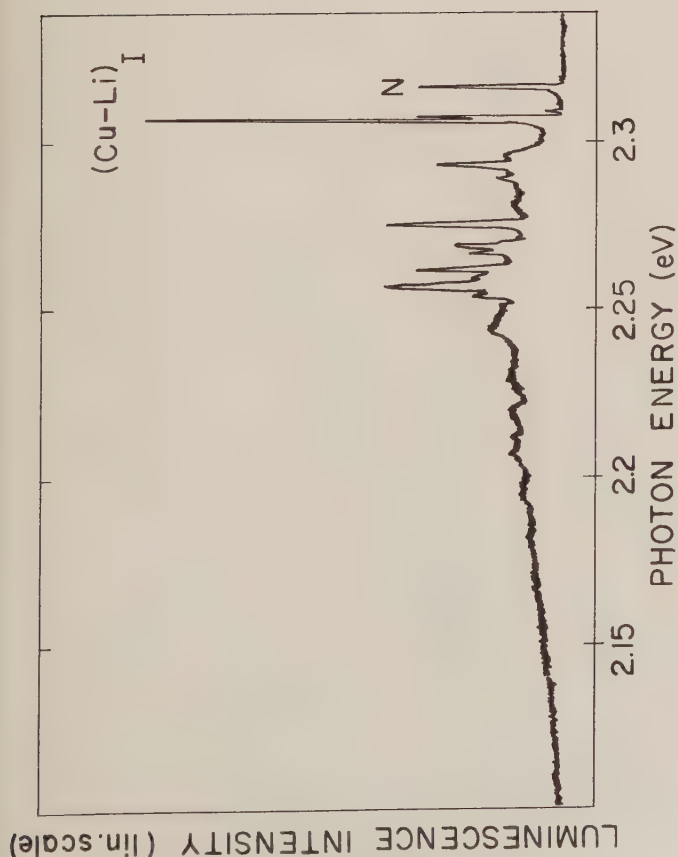


Fig. 2a The photoluminescence spectrum at 2K close to the bandgap, for the same sample as in fig. 2, is seen to be dominated by the $(\text{Cu-Li})_{\text{I}}$ bound exciton [2], and the N-related bound exciton.

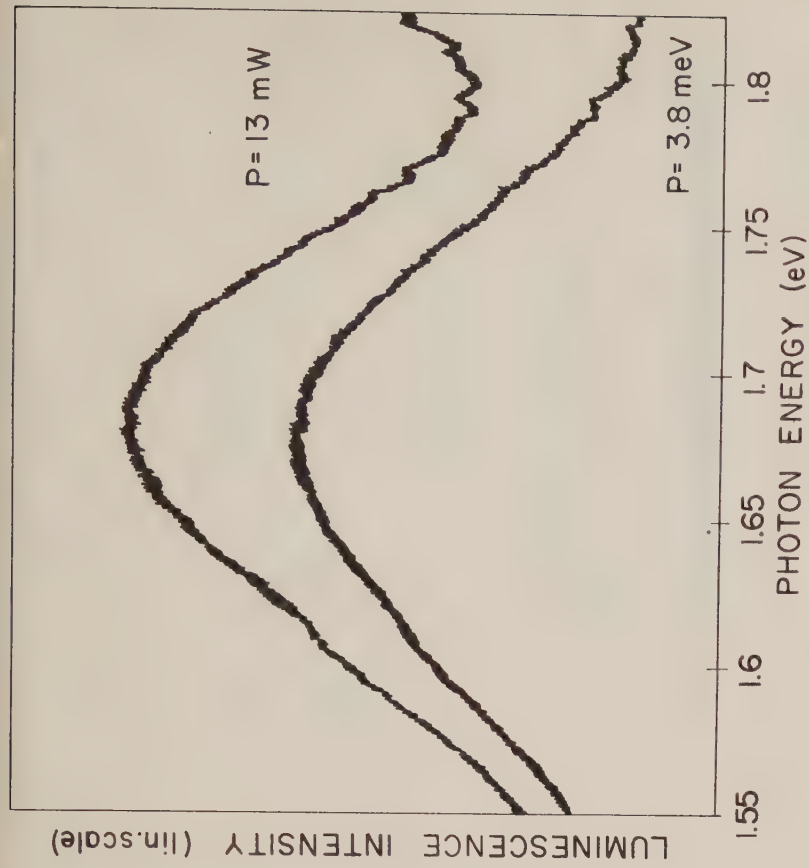


Fig. 2b A comparison of the 1.70 eV emission at two different excitation power densities. A small shift in peak position is observed along with a change in the line-shape. This is believed to be caused by a saturation of an emission at slightly lower energy, at high excitation density.

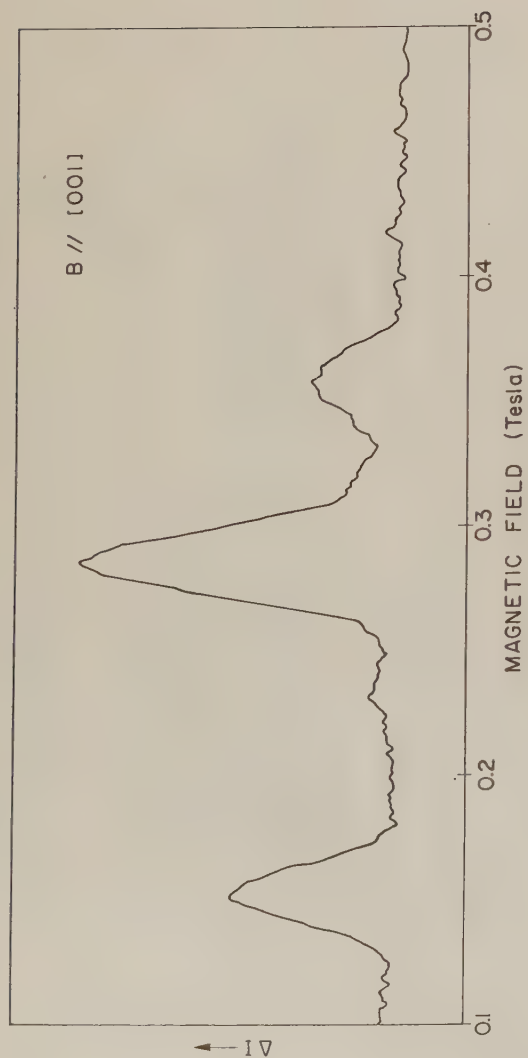


Fig. 3 The well structured ODMR signal for the 1.70 eV band.
At 0.15 T a $\Delta M = 2$ resonance occurs and for $B // [001]$ resonances can be seen for $B \approx 0.3-0.4$ T.

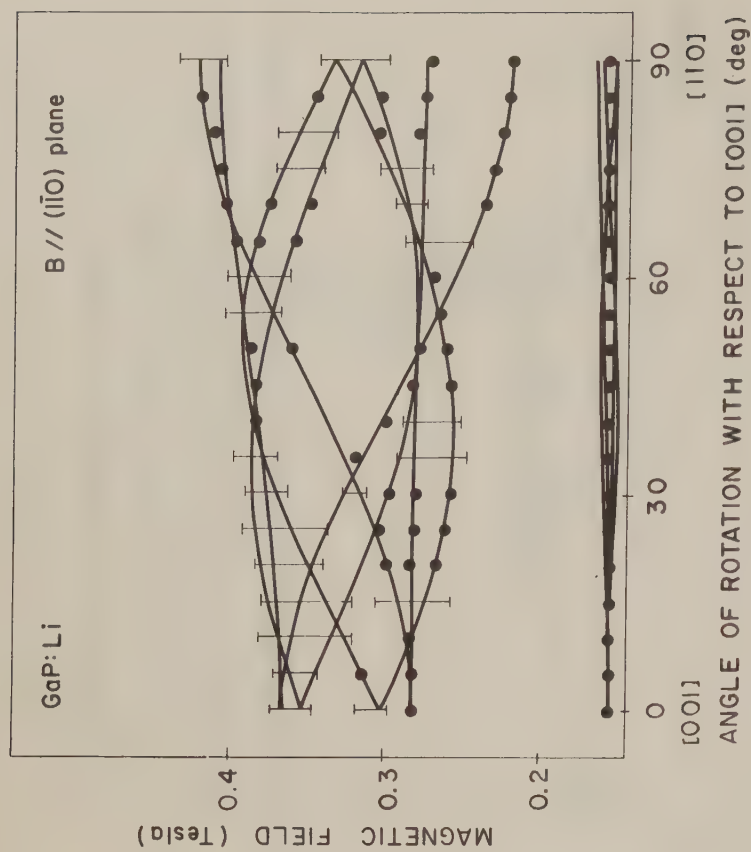


Fig. 4 Angular dependence of the ODMR signal showing a complicated anisotropy pattern, consistent with a defect which is bent in a $[110]$ -plane.

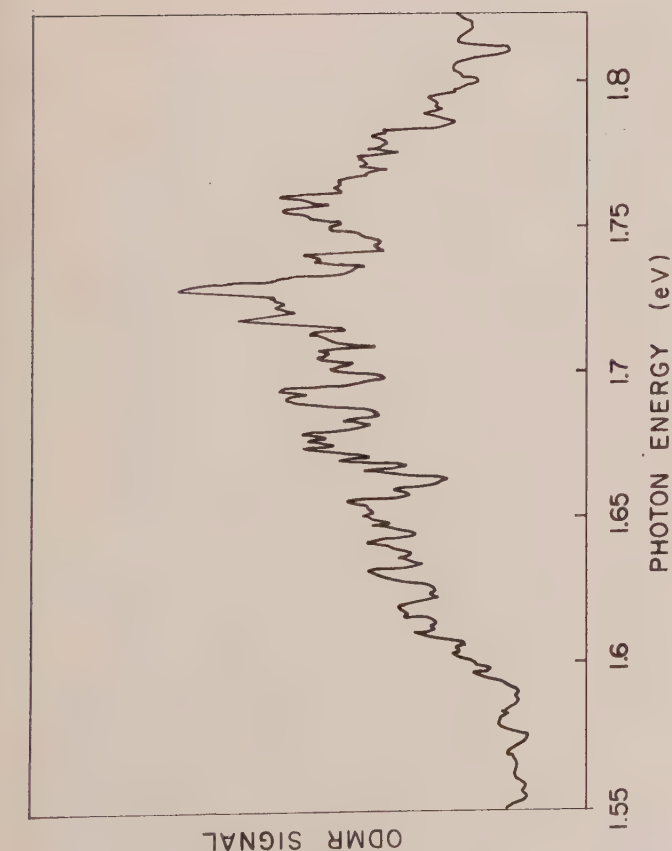


Fig. 5 Spectral dependence of the ODMR signal. As can be seen, the ODMR-PL shape corresponds to the ordinary photoluminescence shape, (Fig. 2b).

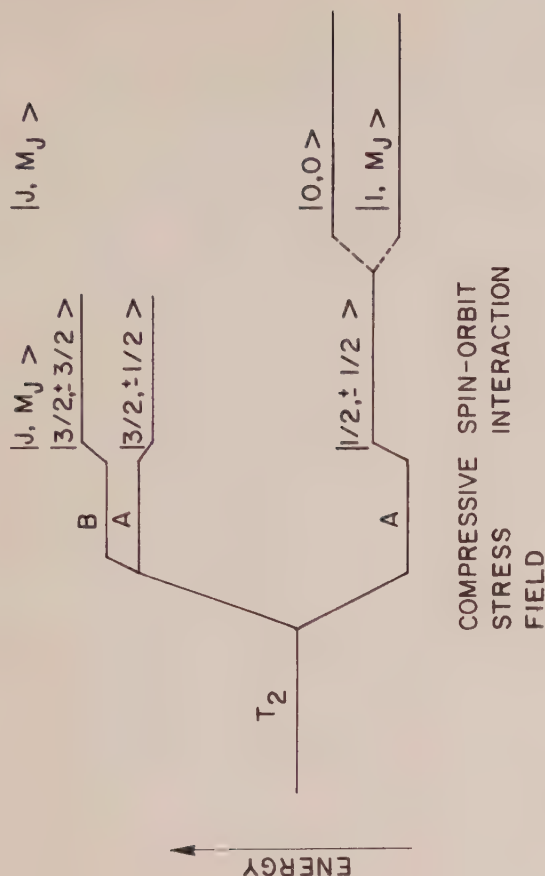


Fig. 6a A schematic figure on the effect of a strong compressive stress field, exceeding that of the spin-orbit interaction, on the electronic states of an exciton. In low symmetry the T₂ hole state (in T_d) is split into three states, labelled A, A, B. These are shifted by the spin-orbit interaction. The $|1/2, \pm 1/2\rangle$ state is lowest in energy. Coupling with an $S = 1/2$ electron gives two states, one singlet and one triplet. The use of J and M_J quantum numbers is not strictly correct but serves as a guide to compare with other defects of higher symmetry.

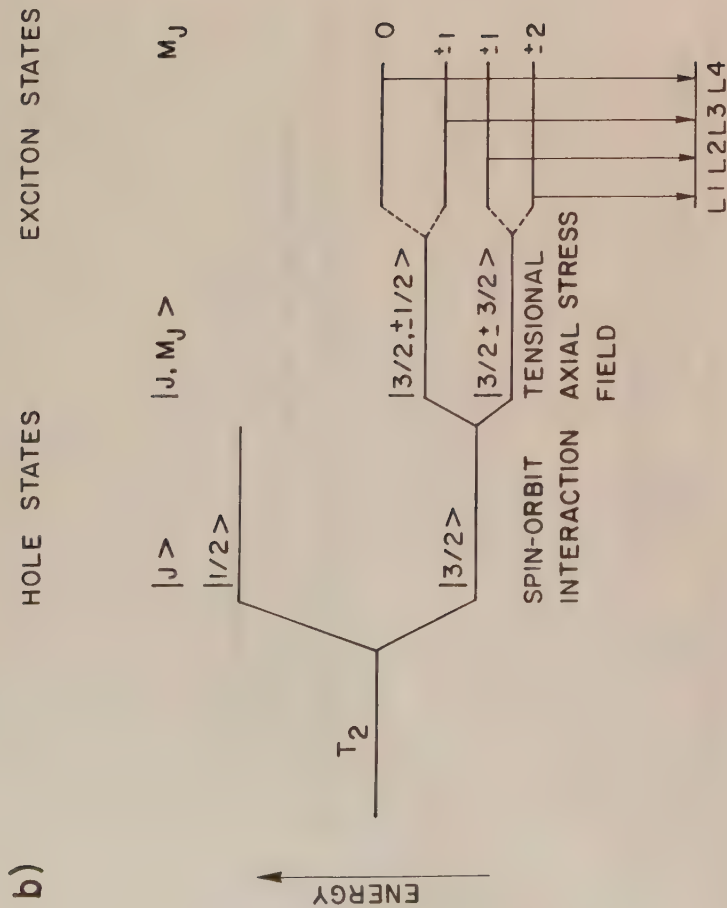


Fig. 6b The effect of a weak tensional axial stress field applied to an exciton. Spin-orbit interaction will split the T_2 hole state into a $J = 1/2$ and a $J = 3/2$ state. The stress field will cause a splitting of the $J = 3/2$ state according to M_J indicated in the figure.

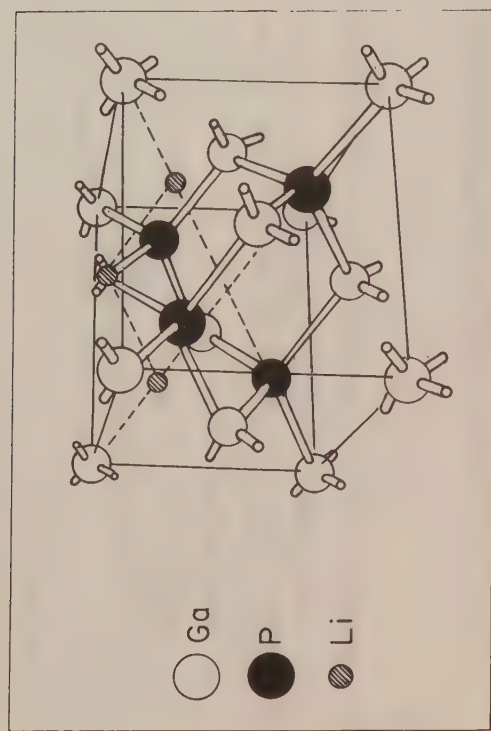


Fig. 7 A possible model of the Li-related defect studied in this work. Li on a Ga-site is surrounded by two interstitial Li. The defect is bent in a $[110]$ -plane as inferred from ODMR data. One Li_i atom might also be displaced off a trigonal axis.

ODMR excitation spectroscopy in GaP

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Abstract. Photoluminescence excitation (PLE) spectra taken in the ODMR mode with tunable laser excitation are discussed. Experimental data are shown for the 1.911 eV Cu-related defect-bound exciton in GaP, illustrating the power of this ODMR-PLE technique in establishing the important connection between an ODMR signal and the defect state experiencing the microwave resonance.

Optically detected magnetic resonance (ODMR) in photoluminescence (PL) has recently become a rather popular technique to investigate electronic excitations at defects in semiconductors (Cavenett 1981). The correlation between an observed ODMR resonance spectrum and a particular defect is usually established by recording the spectral dependence of the PL signal at resonance. In cases where such an ODMR-PL spectrum agrees with the ordinary PL spectrum obtained for the defect under study, this is usually taken as strong evidence for the correlation between the ODMR resonance and this specific defect.

Recent studies indicate that such a procedure can often be quite misleading. In fact we have found from an ODMR study of several Cu-related defects in GaP that an ODMR signal associated with a particular PL spectrum by the above procedure may very well be due to quite different electronic states than the one giving rise to the luminescence spectrum, often even quite different defects give rise to the resonance. Similar experience has been reported by some other researchers (Lee *et al* 1982, Gal *et al* 1979, 1981). One possible reason for this seemingly unsatisfactory situation would be an efficient excitation transfer from the state responsible for the ODMR signal to the emitting one.

In this Letter we report another technique in order to establish the correlation between an ODMR resonance and a particular defect, based on photoluminescence excitation spectroscopy (PLE). In cases where the defect under study possesses several electronic excited states, these states can usually be observed in ordinary PLE by scanning the excitation photon energy, while detecting in the characteristic PL band of the defect. Particularly detailed such spectra have recently been observed for bound excitons related to neutral complex defects in GaP (Monemar *et al* 1982, Gislason *et al* 1982). Such excited states give a selective fingerprint of the particular defect system. (They are on the other hand usually only seen in PLE and not in ordinary transmission data, due to a

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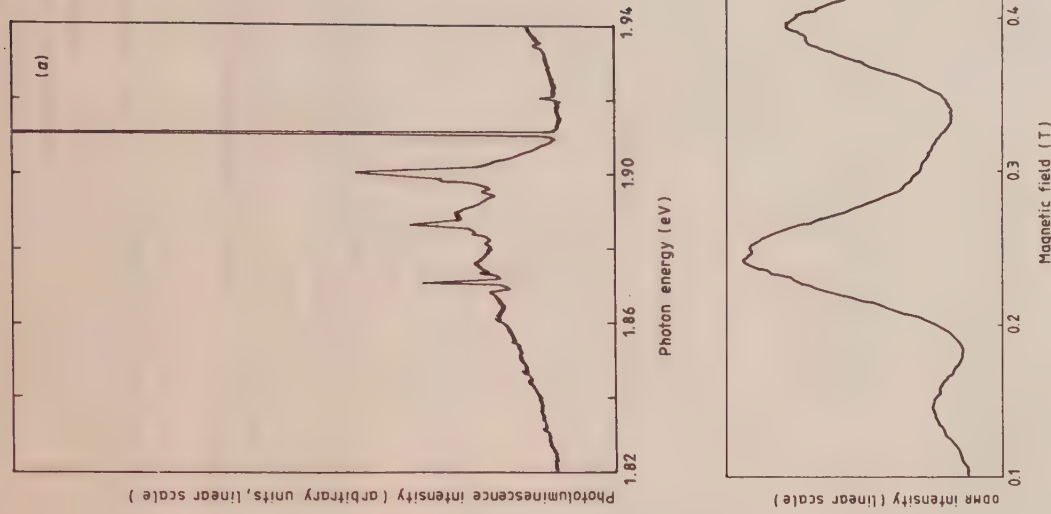


Figure 1. (a) Photoluminescence (PL) spectrum at 2 K of the 1.911 eV bound exciton in GaP, related to a (100)-oriented Cu complex. The electronic line of this PL spectrum is a magnetic triplet, and has a moderately weak phonon coupling as seen in the figure.

(b) ODMR spectrum obtained at 3 K in a Bruker ER 200D-SRC-ODMR system employing a cylindrical cavity at 9.2 GHz with an Oxford ESR 10 cryostat. The entire PL spectrum in figure 1(a) is detected via an edge filter in phase with a chopped microwave excitation of 6 kHz and 200 mW. No polarisers are employed, i.e. the total microwave-induced signal is detected. The dye-laser photon energy is 2.038 eV in this case.

low oscillator strength.) If the same spectrum of excited states for the defect can be seen in a PLE spectrum for the ODMR signal, obtained at microwave resonance for PL in the characteristic emission band, then proof has been obtained that the ODMR signal is specific for the defect under study. If, on the other hand, such a defect-specific excitation spectrum is not observed in ODMR-PLE, the association between the ODMR resonance and the studied defect PL spectrum is in general not established.

To illustrate this point we shall here show experimental data from ODMR of the 1.911 eV Cu-related complex in GaP, previously studied in some detail by optical spectroscopy (Gislason *et al.* 1982). A PL spectrum at 2 K of the lowest-energy BE line of this defect is shown in figure 1(a). A corresponding PL-ODMR spectrum obtained in our laboratory with a 9.2 GHz system is shown in figure 1(b). The ODMR signal is here detected in the PL mode, where the PL signal is recorded by a lock-in technique in phase with the chopped microwave excitation at resonance in the cavity, i.e. only the microwave-induced part of the PL signal is sensed, at a fixed value of magnetic field and microwave frequency. The 1.911 BE line is a magnetic triplet line, isotropic in Zeeman data (Gislason *et al.* 1982). The ODMR resonance shown in figure 1(b) is a total intensity spectrum (no polarisers employed). Two broad peaks dominate, due to overlapping contributions from two triplet resonances associated with each of the inequivalent (100)-oriented defects in the sample, in the orientation employed.

For this particular defect the lowest BE triplet state has quite low oscillator strength compared with a number of excited states associated with the same BE, as shown in ordinary dye-laser-excited PLE spectra in figure 2(a) and (b). Such PLE spectra have been reported previously by Gislason *et al.* (1982), and are understood in terms of excited electronic states of the defect BE, of a different symmetry than the triplet ground state. Using the same dye-laser excitation, in our ODMR equipment, detecting the total intensity of the emission in figure 1(a) at a microwave chopping frequency of 6 kHz around 0.24 T (figure 1(b)), a PLE spectrum is quite easily obtained for the ODMR signal. The resulting ODMR-PLE data are shown in figures 3(a) and (b), for the same photon energy regions as in figure 2. Evidently the spectra in figures 2 and 3 are of identical spectral shape. In addition the ODMR signal-to-noise ratio with selective excitation in the excited states of the defect is very much enhanced compared with the case of above-band-gap excitation.

The close similarities between the PLE curves in figures 2 and 3 permit several important conclusions. In the case shown here, several excited electronic BE states are seen in PLE, a strong singlet at 2.002 eV and other states in the region 2.19–2.24 eV (figures 2(a) and (b)). When the lowest BE state is responsible for the ODMR resonance observed, the relative intensities of the excited states should be the same as in ordinary PLE, if spin-dependent capture is not important simultaneously. Furthermore, the possible occurrence of resonance in one of the excited states simultaneously with the monitored resonance in the lowest BE state detected in the PL signal should significantly distort the intensity (or shape) of the corresponding peak in the ODMR-PLE spectrum. The spectra in figures 3(a) and (b) are typical for the case where only the emitting lowest BE state of the defect is involved in ODMR, and the capture to this state via the excited states is the same in an ordinary PL experiment and in ODMR-PL.

As mentioned above, excitation transfer from other defect states is often a dominant process in ODMR spectroscopy, and an ODMR-PLE spectrum gives direct information on this point. If the ODMR signal detected in a specific PL band actually originates from a quite different electronic state on another kind of defect, the characteristic absorption spectrum of that defect should show up strongly in ODMR-PLE. More importantly, the excited states of the defect responsible for the PL signal detached should not be seen.

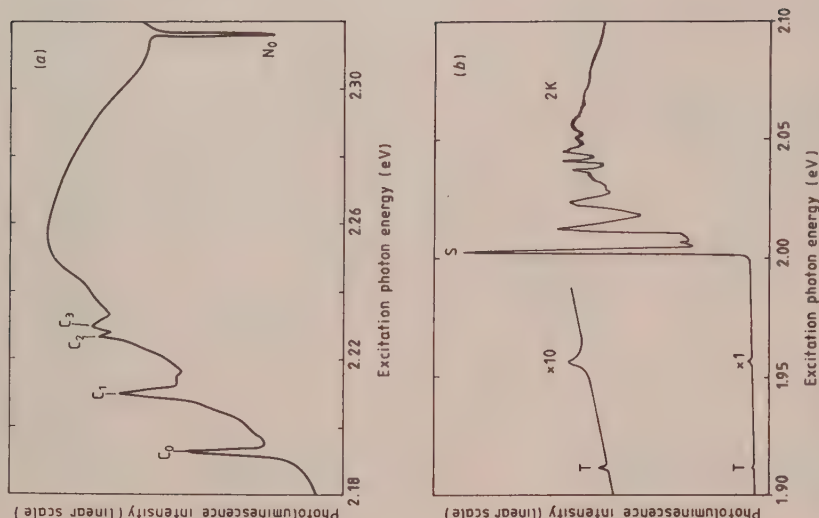


Figure 2. (a) Photoluminescence excitation (PLE) spectrum at 2 K of the 1.911 eV triplet PL emission in figure 1(a), obtained with a Coherent 590 tunable dye-laser, in this case with a Coumarin 540 dye covering the near-band-gap region. Several excited electronic states related to the 1.911 eV defect are seen.

(b) PLE spectrum as in (a), but in another photon energy region covered by the Rhodamine 6G dye. A strong excited state at 2.002 eV, together with a strong phonon wing, is seen, related to the 1.911 eV defect. No states are seen in the intermediate photon energy region not displayed in figures 2(a) and (b).

Defect systems in GaP where this case actually seems to be demonstrated are currently under study in our laboratory (Godlewski *et al.* 1984).

Finally, we point out that similar spectral techniques should be applicable to the case of ODMR detected in absorption via magnetic circular dichroism (MCD-ODMR), where the electronic ground state of a defect-related excitation is sensed (Meyer *et al.* 1984). An optical absorption spectrum with detection of the ODMR signal should in this case provide the fingerprint of the defect state under study, similarly to the case of ODMR-PLE discussed in this Letter.

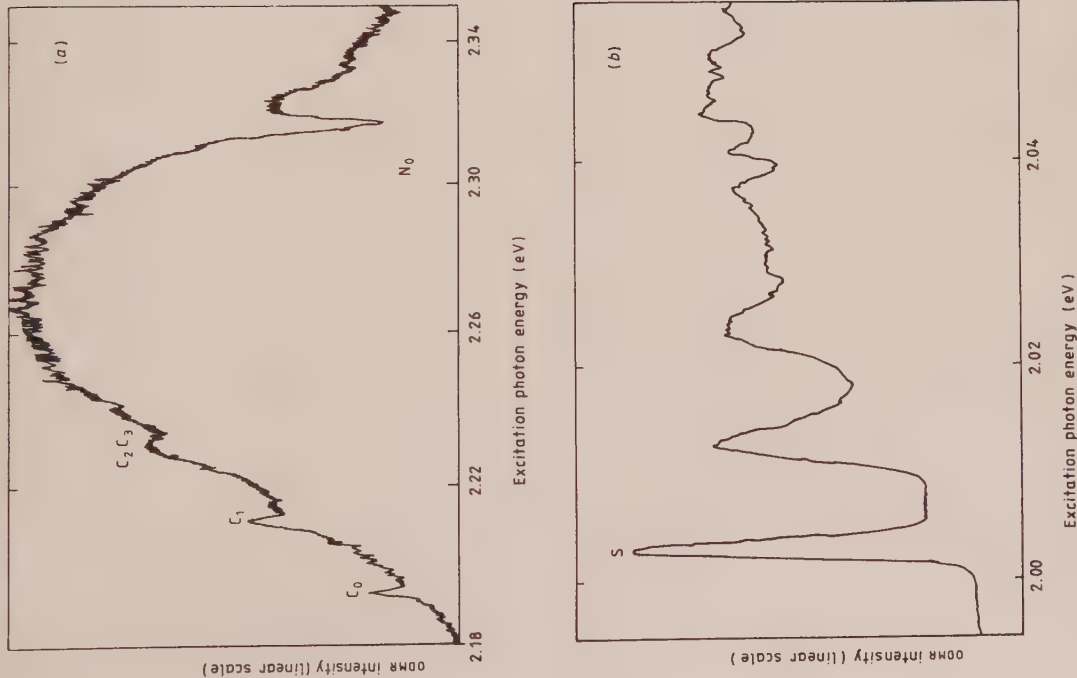


Figure 3. (a) Dye-laser-induced excitation spectrum for the ODMR signal in figure 3(b) employing a Coumarin 540 dye. The magnetic field is set at 0.24 T, at a fixed microwave frequency of 9.20 GHz. The entire luminescence spectrum of figure 1(a) is detected with an edge filter at a microwave chopping frequency of 6 kHz. Note the good agreement with this spectrum and the ordinary PLE spectrum of figure 2(a).
(b) ODMR-PLE spectrum as in figure 3(a), covering the same lower photon energy region as in figure 2(b), employing a Rhodamine 6G dye. Note the similarity with the ordinary PLE spectrum in figure 2(b).

References

- Cavenett B C 1981 *Adv. Phys.* **30** 475-538
- Gal M, Cavenett B C and Dean P J 1981 *J. Phys. C: Solid State Phys.* **14** 1507-18
- Gal M, Cavenett B C and Smith P 1979 *Phys. Rev. Lett.* **43** 1611-4
- Gislason H P, Monemar B, Dean P J, Herbert D C, Depinna S, Cavenett B C and Killoran N 1982 *Phys. Rev. B* **26** 827-45
- Godlewski M, Monemar B, Chen W M and Pistol M E 1984 unpublished
- Lee K M, O'Donnell K P, Weber J, Cavenett B C and Watkins G D 1982 *Phys. Rev. Lett.* **48** 37-40
- Meyer B K, Spaeth J M and Scheffler M 1984 *Phys. Rev. Lett.* **52** 851-4
- Monemar B, Gislason H P, Dean P J and Herbert D C 1982 *Phys. Rev. B* **25** 7719-30

DISORDER-INDUCED ANDERSON LOCALIZATION IN $\text{GaAs}_{1-x}\text{P}_x$

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We report on low-temperature photoluminescence studies of undoped $\text{GaAs}_{1-x}\text{P}_x$ alloys. Arguments are presented for the identification of the strongly asymmetrically shaped peak, called M_0^* , with the recombination of electrons and holes bound to different regions of the alloy. It is proposed that at low temperatures, the carriers are subject to Anderson localization below a mobility edge in the potential wells which are induced by the fluctuating alloy potential. Variations in its properties with varying alloy composition suggest that the localization effects are primarily related to electrons with X -conduction band character.

The study of defects in III-V alloys is achieving considerable interest. Alloying allows the continuous variation of the band structure while the defect is kept constant. In this paper we report on some luminescence studies of undoped $\text{GaAs}_{1-x}\text{P}_x$ where different recombination processes across the cross-over region where the band gap changes from indirect to direct are followed. Special emphasis is put on the investigation of the properties of a low-temperature recombination peak, usually denoted M_0^* , which has been claimed to be related to excitons bound to alloy fluctuations [1]. Data will be presented which suggest that this peak is due to the recombination of electrons and holes which are separated and individually bound in potential wells and which experience Anderson localization due to the fluctuating alloy potential. Furthermore, investigation of zero-phonon and momentum-conserving recombination processes shows strong band-structure enhancement due to inter-conduction-band mixing.

The samples used for this study were grown by the MOVPE technique [2] and were nominally undoped. Residual impurities gave a net carrier concentration of below 10^{16} cm^{-3} . The samples were immersed in a helium bath cryostat (2K) and excited by an argon ion laser using a wavelength of $\lambda=5145 \text{ \AA}$. The spectra were recorded through a Jarrel-Ash 0.75 m double monochromator by an Si photomultiplier and conventional lock-in techniques.

Fig. 1 shows the main emission peaks in the $\text{GaAs}_{1-x}\text{P}_x$ alloys. The band structure has been calculated using the polynomial given by Wolford et. al. [3]. In the composition range where the bandgap is direct the main peaks are identified as the recombination of excitons bound to neutral donors (D_0^*), and conduction-band-to-acceptor (free-to-bound) transitions.

On the indirect side, the luminescence is dominated by excitons bound to neutral donors (D_0^*), and, for low excitation densities, a peak M_0^* , related to alloy fluctuations [1]. M_0^* has a low activation energy (2-3 meV), a long non-exponential decay time (1-100 μs) and an anomalously sharp high-energy cut-off. The binding energy is about 10 meV, measured from the free exciton peak which has an internal binding energy of 22 meV [4]. M_0^* has been interpreted in terms of an exciton bound to composition fluctuations in the alloy [1]. A similar peak has been seen in $\text{CdS}_{1-x}\text{Se}_x$ though with a lifetime of the order of nanoseconds [4].

The spectra (see Fig. 2a) away from the Γ - X transition region are relatively simple to interpret. The direct side emission (exemplified by $x=0.38$ in Fig. 2a) consists of a donor-bound exciton and a free-to-bound (FB) transition. The FB peak saturates at higher excitation densities. Assuming that the D_0^* binding energy is constant [6], the FB transition energy as a function of the composition may be estimated. We find that the acceptor binding energy increases from about 26 meV for $x=0$ to 36-37 meV for $x=0.38$. This extrapolates to a binding energy of about 39 meV for $x=0.45$.

For indirect band gap compositions two emissions are observed (at 2K). Besides the donor-bound exciton (D_0^*), another peak, M_0^* , with quite different properties appears on the high energy side. The energy difference between D_0^* and M_0^* is fairly constant, 7-11 meV, with a small tendency for M_0^* to become deeper with decreasing x . With a binding energy of 41 meV for D_0^* , the binding energy of M_0^* is 32 meV.

It can be seen in Fig. 3 that the electronic states as well as the nature of the radiative recombination change considerably

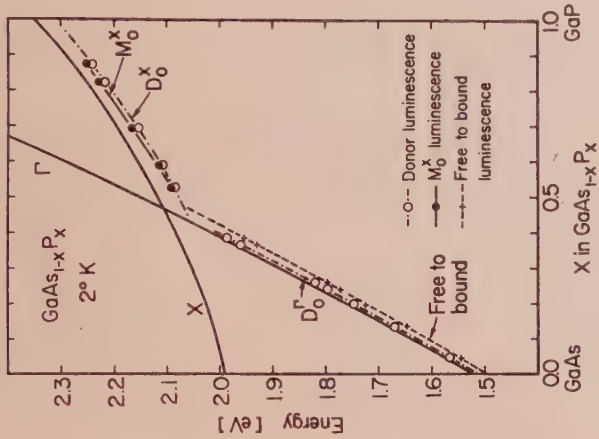


Fig. 1. Diagram showing the main peaks plotted as a function of composition with the valence band edge as a reference. Shown are the free-to-bound emission and the donor-exciton (D_0^*) emission on the direct side. On the indirect side, the donor-bound exciton (D_0^*) emission and the M_0^* peak are indicated.

over the small range of composition covered, $0.45 < x < 0.50$, around the Γ - X cross-over. Three more peaks (S, P and T in Fig. 3) are seen. They will be subject to further investigation.

Fig. 2a shows the spectral variation and the dependence on the excitation density for alloys of different compositions. The result of an investigation of the saturation behaviour of M_0^* and D_0^* is shown in Fig. 2d. The behaviour of M_0^* is clearly distinguishable from that of D_0^* . Another observation (Fig. 2) is that D_0^* decreases in intensity compared with M_0^* at constant laser intensity when the cross-over point is approached. This is most pronounced close to $x=0.50$ but D_0^* can still be followed to $x=0.49-0.49$. It is then difficult to calibrate the M_0^* binding energy which amounts to finding the x -value of the particular spot on the sample which is being measured. One can, however, still find the M_0^* peak since it shows saturation behaviour although it requires higher laser intensities.

On the direct side of the cross-over point M_0^* rapidly decreases in intensity and the,

partly overlapping, P emission becomes dominant. Although we are unable to observe the behaviour when M_0^* emerges from the Γ conduction band, it seems clear that the existence of the M_0^* peak is related to the X -conduction-band minimum.

For all compositions with $x > 0.48$ the M_0^* luminescence peak has a very rarely observed line-shape. The high-energy side displays an extremely sharp cut-off, with a transition region (90%-10%) of $\approx 1 \text{ meV}$. This can be compared with $\approx 10 \text{ meV}$ for D_0^* and $\approx 6 \text{ meV}$ for D_0^* .

We propose that the observed properties of M_0^* may be explained by charge carriers being localized in the low-density-of-states (DOS) tail induced by the randomly fluctuating potential of $\text{GaAs}_{1-x}\text{P}_x$ [7]. The prerequisite for Anderson localization seems to be fulfilled, i.e. two potentials with different depths (As and P) being randomly positioned on the fixed lattice sites of the group V sublattice. For sufficiently low density-of-states in the low-energy tail (see Fig. 2b), the carriers become trapped, however only up to an energy, the mobility edge, where they, according to Mott [7], abruptly become delocalized and mobile. The saturation behaviour of M_0^* in Figs. 2a and 2d may now be simply explained (see Fig. 3b). With increasing excitation density the population of states in the density-of-states up to the mobility edge increases uniformly, leading to, as observed, an unchanged line-shape. This observation is in agreement with the suggestion that the carriers are trapped in non-interacting wells with no transfer between the wells. Once the DOS is filled, the M_0^* peak saturates. Lai and Klein [1] suggested that the high-energy cut-off of M_0^* is due to a competing non-radiative recombination above a certain threshold. However, we think that it is difficult to imagine the observed sharp profile without invoking the dramatic effects of localization.

Saturation of the tail states is quite easily achieved since the lifetime of the states is very long, 1-100 μs , compared with a few ns for other band-edge emission lines. We observe, in agreement with Lai and Klein [1] that the decay of M_0^* is non-exponential. As a result of the findings in the present study we propose that M_0^* is not due to excitons but to the recombination of electrons and holes which are trapped in potential wells at different locations in the alloy. Hence, the overlap of electron- and hole wave-functions will be small, which leads to long decay times, and the recombination rate will vary with the electron-hole overlap, leading to non-exponential decay. Thermal quenching is explained by excitation from the population of trapped states up to the mobility edge followed by recombination via other channels. The line-profile should shift towards lower energy at higher temperatures, which has been observed by Lai and Klein [8]. An estimation of the energy separation between the centre of gravity of the M_0^* line-profile and the suggested mobility edge gives $\approx 5 \text{ meV}$, and to be compared with the thermal quenching activation energy of 2-3 meV.

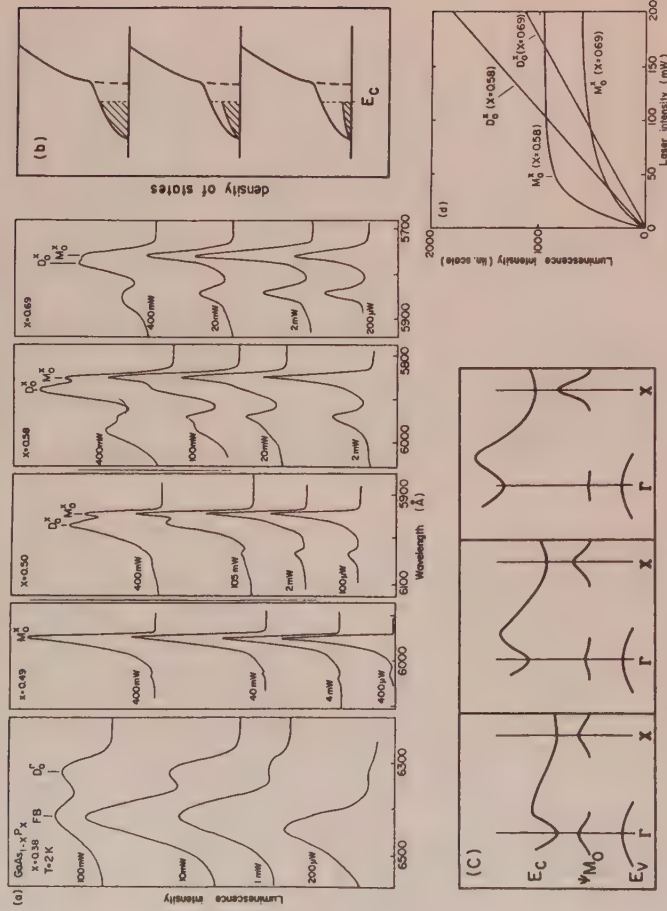


Fig. 2. (a) Spectra of the M_0^x , D_0^x , $D_0'^x$ and free-to-bound peaks, for different compositions and different laser intensities. Notice the sharp high-energy cut-off of the M_0^x peak and the different intensities of D_0^x and M_0^x for different compositions. The EB peak saturates at higher laser intensities. (b) A schematic description of our interpretation of the anomalous lineshape, the thermal quenching and the saturation behaviour of M_0^x luminescence in terms of localized and non-interacting states which are localized below the mobility edge (E_C) due to a random potential in a perfect lattice. (c) Qualitative behaviour of the GaAs_{1-x}P_x band-structure-enhanced quasi-direct M_0^x recombination. (d) The excitation power dependence of the emission intensity of the D_0^x and M_0^x luminescence peaks.

The disappearance of the M_0^x line for $x < 0.46$ where the band structure becomes direct, is in qualitative agreement with our interpretation of the M_0^x peak. Although the potential fluctuations are expected to be similar in the direct and indirect regions, it

is more difficult to localize Γ -conduction-band electrons with much smaller effective masses than the x band minimum and, correspondingly, more extended wavefunctions. In a very simple model the relatively heavy holes are localized to a point while the lighter electrons are

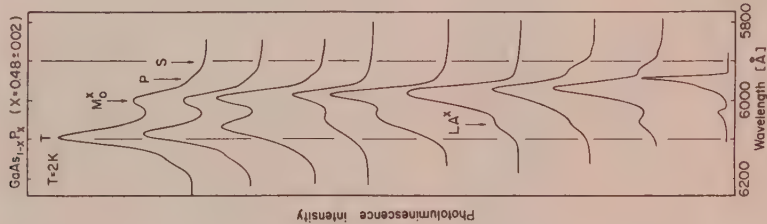


Fig. 3 A detailed plot of the photoluminescence spectra obtained in the narrow composition region ($0.46 < x < 0.50$) around the direct-indirect crossing.

REFERENCES

1. Shui Lai and M.V. Klein, Physical Review Letters **44**, 1087 (1980).
2. L. Samuelson, P. Omling, E. Titz, H.G. Grimmeiss, Journal de Physique **12**, C5-323 (1982).
3. D.J. Wolford, J.A. Bradley, K. Fry, J. Thompson and H.E. King, Proc. 11th Int. Symp. on GaAs and related compounds, Alberquerque, Sept. (1982).
4. M.D. Sturge, A.F. Vink and F.P.J. Kuipers, Applied Physics Letters **32**, 49 (1978).
5. E. Cohen and M.D. Sturge, Physical Review B **25**, 3828 (1982).
6. D.J. Wolford, B.G. Streetman, Shui Lai and M.V. Klein, Solid State Communications **32**, 51 (1979).
7. N.F. Mott and E.A. Davies, "Electronic Processes in Non-crystalline Materials", Oxford University Press, Oxford, second edition (1979).
8. Shui Lai and M.V. Klein, Physical Review B **29**, 3217 (1984).

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It is clear from Fig. 2a that the coupling of M_0^x to LA^x phonons decreases when the composition approaches that of the Γ - x transition. Simultaneously the intensity of the M_0^x emission increases. An explanation of this general behaviour is illustrated in Fig. 2c. For high values of x where the band structure mimics that of GaP, M_0^x is dominated by x -band wavefunctions. It thus has a low probability of decaying without a momentum-conserving phonon, in this case LA^x . Closer to the Γ - x transition, an increasing proportion of the wavefunction is derived from the Γ band, induced by the coupling via the alloy-induced fluctuating potential to conduction-band states, which has a term proportional to $1/|E_\Gamma - E_x|$. This quasi-direct recombination gains in importance relative to the momentum-conserved recombination. Indeed, we observe a corresponding reduction in the radiative decay time of M_0^x to < 1 ns for $x=0.48$.

localized by a square well of depth V_0 . Ignoring Coulomb attraction, the binding energy, E_b , which is what can be determined experimentally, is greater for a well with a greater depth. The extension of the electron wave function outside the well, given by $\Psi \sim \exp(-\alpha r)$, then has a strong dependence on α . Since $\alpha \sim \sqrt{E_b}$, a more deeply bound electron is more localized, and should recombine more slowly, which is indeed what has been observed (8). If Coulomb attraction had the major influence, the more deeply bound pairs would be the closest pairs and should have the shortest lifetime, which is in disagreement with experiment. In this model the binding energy is less if the electron mass is smaller leading to a much smaller number of localized electrons. It is then correspondingly more difficult to observe the M_0^x emission for lower electron mass, that is, for the direct band gap. The extension of the wavefunction as a function of energy and mass can be treated much more carefully for disordered systems, but the result is the same as above (7).

PHOTOLUMINESCENCE STUDY OF LOCALIZATION EFFECTS INDUCED
BY THE FLUCTUATING RANDOM ALLOY POTENTIAL IN INDIRECT
GAP $\text{GaAs}_{1-x}\text{P}_x$

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PHOTOLUMINESCENCE STUDY OF LOCALIZATION EFFECTS INDUCED BY THE FLUCTUATING
RANDOM ALLOY POTENTIAL IN INDIRECT GAP $\text{GaAs}_{1-x}\text{P}_x$

Abstract

In the recombination spectra of indirect band-gap alloys of $\text{GaAs}_{1-x}\text{P}_x$ a peculiar and asymmetric luminescence band, M_0^x , has previously been reported to be due to a fluctuating alloy potential. Detailed experiments are reported here on $\text{GaAs}_{1-x}\text{P}_x$ samples which exhibit exceptionally strong M_0^x luminescence. The properties and line-shape of M_0^x have been studied as a function of sample composition, excitation power densities and decay times. It is concluded that recombining electron-hole pairs are trapped by the fluctuations of the band-edges which form exponential tails in the gap and that the charge carriers are subject to localization below a mobility edge. Calculations performed using this model are able to explain most of the observed behaviour of the M_0^x emission band.

1-. Introduction

The composition disorder in III-V semiconductor alloys induces different effect observable by luminescence⁽¹⁻⁵⁾. On the one hand, the impurity bound exciton lines are inhomogenously broadened, on the other hand, excitons bound to nitrogen impurities become deeper than donor bound excitons with decreasing composition in $\text{GaAs}_{1-x}\text{P}_x$. The large k components of the fluctuating potential breaks the k selection rules^(6,7), making the zero phonon transitions allowed in indirect band gap compounds. The random potential induces localized states which give rise to a luminescence band (M_0^x), with unusual properties appearing 7 to 12 meV below the free exciton. This band has been interpreted either as the recombination of a localized exciton^(8,9), (i.e. the electron and hole have the same origin in space), or as the recombination of a localized electron and a localized hole, trapped in different potential wells⁽¹⁰⁾. The lifetime of the M_0^x luminescence band is very long (5-100 microseconds) and strongly non-exponential. Such recombination of localized electron-hole pairs have been reported in a number of alloys under particular experimental conditions⁽⁷⁻¹¹⁾, namely low temperatures and low excitation power densities.

In this paper, we present experimental results on $\text{GaAs}_{1-x}\text{P}_x$. We have studied the evolution of luminescence spectra with temperature, excitation power, time and composition, x, in order to obtain a better characterization of these states. Dye-laser experiments have been used to study resonant luminescence excitation and to measure the luminescence line-shape, revealing an exponentially varying density-of-states in the band-gap.

The samples used for this study were grown by the MOVPE technique⁽¹²⁾, and were nominally undoped. Residual impurities gave a net carrier concentration $n \leq 10^{16} \text{ cm}^{-3}$.

The luminescence spectra of $\text{GaAs}_{1-x}\text{P}_x$ for different compositions: $x = 0.51$, $x = 0.52$, $x = 0.56$, $x = 0.61$, $x = 0.85$, at $T = 2\text{K}$ and for excitation power $P = 40 \text{ mW/cm}^2$ are shown in Fig. 1. The M_0^x peak is assigned to the zero phonon line due to carriers localized by the fluctuating potential. The IA_M^x phonon replica of M_0^x is labelled M_1^x . The IA_M^x phonon energies for different compositions, x , are given in Table 1. In addition to the IA_M^x phonon replica we also observe the TA_M^x (13 meV) and the TO_M^x (47 meV) phonon replicas of M_0^x , for the composition $x = 0.85$ (Fig. 1e). At higher excitation power densities, the D_0^x and D_1^x peaks, assigned respectively to the donor bound excitation level and its IA_D^x phonon replica are observed (Fig. 2). The relative intensities $I_{D_1^x}^x / I_{D_0^x}^x$ and $I_{M_1^x}^x / I_{M_0^x}^x$ are similar and seem, hence, not to depend on the degree of localization.

II-. Variation with excitation power densities

Fig. 3 shows the intensity variation $I_{M_0^x}$ with excitation density P for different compositions: $x = 0.51$, $x = 0.52$, $x = 0.56$, $x = 0.85$. The intensity variation is linear for small P ($P < 0.1 \text{ W/cm}^2$) and saturates already at $P \sim 1 \text{ W/cm}^2$. At saturation, the intensity $I_{M_0^x}$, which depends on the composition (Fig. 3), is the product of a density ρ and a probability for radiative recombination W . Here ρ would be the integral of the density of states, per unit energy, in the localized tail, below a mobility edge. The dependence of W on composition will be deduced later in section IV from the time decay measurements.

Fig. 4 shows the variation of $R(x) = \frac{I_{M_1^x}}{I_{M_0^x}}$ with composition x for different excitation power densities. $R(x)$ increases when x is increased from $x = 0.5$

to $x = 1.0$, and $R(x)$ depends strongly on the band gap structure of the alloy, a so called band-structure enhancement effect⁽¹⁰⁾. Actually, for a sample with $x = 0.49$ the M_1^x replica is very hard to even observe.

Fig. 5 shows different behaviour with excitation power densities of the M_0^x , M_1^x , D_0^x and D_1^x peak intensities. The variation is linear for D_0^x and D_1^x in the whole excitation range while there is saturation at relatively low power densities ($P \geq 1 \text{ W/cm}^2$) for M_0^x and for M_1^x already observed in Fig. 3.

An important result from the data in Fig. 5 is that the M_0^x intensity clearly saturates and does not change from a linear to square-root dependence on power densities. This is in contradiction to the results reported by Lai and Klein⁽⁹⁾ who interpreted such a change of the slope as being indicative of an Auger process of bi-excitations. It is also worth noting that the saturation of M_0^x in our samples sets in for excitation power densities exceeding those observed by Lai and Klein^(8,9) by, at least, a factor 10. The implication of this difference will be discussed below (Section VII).

III-. The line-shape of M_0^x

As pointed out previously⁽⁸⁻¹⁰⁾ the M_0^x peak has an unusual asymmetric shape, (Fig. 6) with a shape high-energy side. The energy of this high energy cut-off may correspond to the separation of localized and delocalized states of particles responsible for the luminescence⁽¹⁰⁾. The less steep slope on the low-energy side has been suggested to reflect primarily the density-of-states in the tail region.

The result of careful measurements of the M_0^x line-shape, where resonant dye-laser excitation has been used, is shown in Fig. 6 for $x \approx 0.49$, a sample for which M_0^x dominates and D_0^x is not interfering for the excitation densities used. This semi-logarithmic plot shows that the line-shape on the low-energy side is well described by an exponential function, as expected

for a density of states tail caused by a fluctuation potential. The slope of the fitted line gives $\rho(E) \propto e^{E/E_0}$ with $E_0 \approx 7$ meV. This experimentally determined photon energy dependence of the M_0^x line-shape will later (Section VI) be used to calculate temperature and delay-time dependence of the M_0^x line.

IV-. Time dependence of M_0^x

Detailed measurements of the luminescence decay for samples with different compositions x are presented in Figs. 7 and 8. The luminescence decay of M_0^x peak is nonexponential, and its lifetime ($\tau_{M_0^x} \approx 5-100$ μ s) is considerably longer than the D_0^x exciton lifetime ($\tau_{D_0^x} \approx 200$ ns). Fig. 7 shows that the luminescence decay of M_0^x becomes slower when the composition increases.

The dependence of luminescence decay with excitation power is shown in

Fig. 8. The intensity decays more rapidly with increasing excitation power. At saturation, the $I_{M_0^x}$ decay is still non-exponential.

The time decay of a localized electron-hole pair in an indirect gap alloy has been treated by Klein et al.⁽⁷⁾ A non-exponential decay is found due to mixing of Γ -states by the random potential. The distribution of decay rates was given as:

$$P(W) = \langle W \rangle_{av}^{-1} e^{-\frac{W}{\langle W \rangle_{av}}} \quad (1)$$

$\langle W \rangle_{av}$ is the mean radiative decay rate without phonon assistance if the conduction band minimum does not occur at the X -point. $\langle W \rangle_{av}$ is a function of the degree of disorder in the alloy. The one-phonon radiative decay rate W_0 involving momentum conserving phonons is independent of the degree of disorder since it is not sensitive to mixing of Γ -states.

We interpret Fig. 8 by considering that the fast decay of $I_{M_0^x}$ with decreasing composition x corresponds to an increase of $\langle W \rangle_{av}$ with decreasing ener-

which is expected to be large in the mid-alloy range. As a consequence, the ratio $R = \frac{I_{M_1^x}}{I_{M_0^x}}$ which is proportional to $\frac{W_0}{\langle W \rangle_{av}}$, decreases with decreasing composition x and increases with decreasing power densities for a given composition (Fig. 4). We can understand the increasing R with decreasing power excitation by assuming that the population of states requiring a phonon to decay has a different intensity dependence than the states which can decay without phonon assistance. Those states which require phonon participation for their recombination decay slower and, hence, saturate for lower power densities.

V-. Temperature dependence of M_0^x

Figs. 9 and 10 show the evolution of the luminescence spectra with temperature for $x = 0.85$ and $x = 0.51$, respectively. The M_0^x and M_1^x peaks shift to lower energies when the temperature increases from 2K to 8K, but the D_0^x and D_1^x peak energies do not change. The shift is about 4.5 meV for $x = 0.85$ and somewhat larger (about 6 meV) for $x = 0.51$ due to overlap with D_0^x (Fig. 11). For $T > 10$ K, M_0^x and M_1^x peaks are not observed. D_0^x and D_1^x shift to lower energies much faster than the indirect gap E_g^x when the temperature is varied from $T = 10$ K to $T = 23$ K. This shift of the D_0^x -line might be due to thermal de-population of the high-energy portion of the alloy broadened D_0^x energy distribution. Estimates of the energy difference between the M_0^x -line and the free-exciton energy (at low temperatures) gives a scatter in the value of $\Delta(E_g^x - M_0^x)$ between 7-12 meV.

VI-. Model and calculation of time and temperature dependence

In section V, it was shown that the M_0^x -line varies strongly with temperature. Firstly, the energy position shifts approximately linearly with temperature with $\frac{dE}{dT} \approx 0.8$ meV/K. Secondly, the intensity of the peak is rapidly quenched even for very low temperatures with an apparent activation energy of 2-4 meV⁽⁹⁾. We will show here that by using the exponential line-shape

determined in section III and a simple model, where the low temperature high-energy side of the peak is a mobility edge causing the quenching, we are able to generate the reported behaviour of the $\dot{M}_0^x$ peak including the variation of decay times with emission photon energies⁽⁹⁾.

For the model calculations we assume that for each photon energy (E) in the peak the intensity can be written as:

$$I(E, T, t) \propto \rho(E) \cdot e^{-t/\tau_{\text{tot}}(E, T)} \frac{\tau_{\text{tot}}(E, T)}{\tau_{\text{rad}}} \quad (2)$$

where $\rho(E) \cdot e^{-t/\tau_{\text{tot}}(E)}$ is the concentration of occupied states at energy E and time t. We will for simplicity assume that the radiative recombination rate is independent of temperature T and energy E, which is a fairly good approximation although deeper laying states can be expected to be somewhat slower just like what can be expected for more distant electron-hole pairs.

If we tentatively assume that the dominant non-radiative depopulation mechanism consists of thermal excitations from E to a critical E_c at which the excited particles become mobile and may recombine elsewhere, i.e. mobility edge, we can write

$$\tau_{\text{tot}} = \left[\frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{non-rad}}} \right]^{-1} = \left[\frac{1}{\tau_{\text{rad}}} + \nu \cdot e^{-\frac{E - E_c}{kT}} \right]^{-1} \quad (3)$$

As will be shown below we are able to identify the mobility edge E_c with the steep high-energy side of $\dot{M}_0^x$ observed for very low temperatures. τ_{rad} is experimentally determined and ν , an effective frequency for thermal excitation attempts, is the only fitting parameter.

Fig. 12 shows calculated $\dot{M}_0^x$ line spectra as a function of T, with a rapid shift to lower energies accompanying the thermal quenching. For $x = 0.5$ we have $\tau_{\text{rad}} \approx 20 \mu\text{s}$ and the frequency factor $\nu = 2 \cdot 10^8 \text{ s}^{-1}$ has been chosen to give agreement with the experimentally measured peak position shift. The

peak position which has been plotted in Fig. 13a shifts linearly with increasing temperature in agreement with experimental observations. The amplitudes calculated in Fig. 12 have been plotted semi-logarithmically in Fig. 13b in order to determine an apparent activation energy for the thermal quenching for comparison with experimental estimates. Fig. 13b gives an apparent activation energy of $\sim 3 \text{ meV}$, in excellent agreement with published⁽⁹⁾ as well as with unpublished results.

The question, however, arises whether this agreement can only be found in the model where the quenching energy is identical to a mobility edge forming the low-temperature high-energy side of the peak. Attempts to calculate spectra assuming that the thermal quenching occurs via higher lying states as has previously been suggested gives non-linear shifts with temperature and higher activation energies, in disagreement with experiments.

The thermal quenching behaviour should probably not be described by an exponential activation. As shown in Appendix A the shift of the peak position as well as the peak intensity varies, for an exponential density-of-states distribution, approximately linearly with T according to the model used (Eq. (2)).

It has been reported⁽⁹⁾ that the decay rate of the $\dot{M}_0^x$ line varies depending on which portion of the line is studied. The parameters used in the calculated figures above have by Eq. (2) been used to generate the time-dependences shown in Fig. 14a and plotted for different positions around the peak in Fig. 14b. The qualitative behaviour is very similar to that experimentally found by Lai and Klein⁽⁹⁾, lending further support to the model proposed.

VII-. Discussion

In this section we will collect the information that can be gained from the experimental data presented in Sections I to V, from the model calculation

tions in Section VI and from difference in the behaviour of the samples studied here and samples investigated by other groups.

The saturation behaviour displayed in Fig. 3 is qualitatively different from the reported previously⁽⁹⁾, where only the onset of saturation was observed. The data in Fig. 5 do therefore not support the suggestion that the saturation is due to Auger recombination of bi-excitons. Furthermore, the power density level at which saturation starts seems to depend strongly on the doping level of the samples. A comparison between the samples studied in this work and those previously investigated^(8,9) shows that our samples with 10 times lower donor doping levels saturate first at ~ 10 times higher power densities. We think that saturation depends on the density of states $\rho_{M_0^x}$, which can only recombine with the long life-time giving rise to the M_0^x luminescence. Since this luminescence recombination is very slow we suggest that only those low potential regions which do not contain any donors can contribute to the M_0^x luminescence. The concentration of states with long life-time should therefore be larger in our samples and saturation is then expected at higher power density levels. A rough estimate of the dependence on the donor concentration can be made, by noting that the probability of not finding a donor in a well of radius r is given by

$$P \text{ (no donor in well)} = e^{-\frac{4\pi r^3 N_d}{3}} \quad (4)$$

The observed differences gives:

$$\frac{I_{M_0^x}(N_{d_1})}{I_{M_0^x}(N_{d_2})} = e^{-\frac{4\pi r^3}{3} (N_{d_1} - N_{d_2})} \quad (5)$$

which suggests an average radius $\langle r \rangle \sim 200$ Å, which would be a measure of the extent of the localized wave-function.

The observation of this doping dependence of the M_0^x saturation suggests two possible interpretations of the high-energy edge of the M_0^x line. In one case (A) the edge is intrinsic in nature, a mobility edge, and the change in saturation conditions corresponds to a reduced effective M_0^x concentration equal to an increase in the concentration of potential wells with donors inhibiting the slow M_0^x recombination to be observed. In this case the position of the M_0^x line relative to E_g^x and D_0^x is independent of the donor concentration and the faster saturation corresponds to the lower number of M_0^x -defects. In the other case (B) the high-energy edge corresponds to that energy for which the extension of the localized state has a high probability of overlapping with a donor. Since this critical extent must decrease with increasing donor concentration one would expect the critical energy to shift to lower energies (closer to the D_0^x peak) for increasing donor concentrations. However, in this case, the "active" M_0^x defects ought to become saturated at the same power level independent of N_d .

Within experimental accuracy the energy position of M_0^x (relative to D_0^x) is identical in our samples and in those investigated by Lai and Klein. From all observations we therefore conclude that case A with a mobility edge of intrinsic nature seems to be the most likely origin of the anomalous high-energy edge. It would, however, be very useful to study the M_0^x peak position at very low temperatures, say < 1 K (compare calculated results in Fig. 12), in comparable samples of varying N_d .

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Appendix A

Analytical solution for the shift of the peak position with temperature and for the thermal quenching rate:

With the line-shape given in Section V for the M_0^X -peak due to the recombination of disorder trapped carriers we can solve for the energy position and for the amplitude of the peak, i.e.

$$I(E) = \rho(E) \cdot \tau_{tot} \propto e^{E/E_0} \left[\frac{1}{\tau_{rad}} + \nu \cdot e^{\frac{E-E_0}{kT}} \right]^{-1} \tag{A1}$$

$\frac{dI}{dE} = 0$ gives the approximate solution

$$E_{max} \approx E_C - kT \cdot \beta \tag{A2}$$

where β is a function which varies slowly with temperature and can be evaluated for a typical temperature being investigated, T' :

$$\beta \approx \ln \left[\tau_{rad} \cdot \nu \cdot \frac{E_0}{kT'} \right] \tag{A3}$$

Solving for the expected temperature dependence of the peak amplitude shows that the thermal activation energy that can be estimated from a plot of the logarithm of $I_{M_0}^X$ vs $1/T$ is only an approximation. A more careful treatment suggests that for a density-of-states which varies exponentially with energy, it is more relevant to plot the logarithm of $I_{M_0}^X$ vs T ,

$$\ln I_{M_0}^X \approx A - \frac{\beta kT}{E_0} \tag{A4}$$

with β defined as above (Eq. A3).

TABLE 1.

x	0.51	0.52	0.56	0.61	0.85
LA_M^X (meV)	30.5	30.6	30.8	30.8	31.2

The energy of the LA_M^X phonon replica for different alloy compositions, x.

References

1. O. Goede, D. Hennig and L. Johr
Phys. Stat. Sol. (b) 96, 671 (1979)
2. L. Samuelson, S. Nilsson, Z.G. Wang and H.G. Grimmeiss
Phys. Rev. Letters, 53, No. 115, 1501 (1984)
3. D.J. Welford, B.G. Steetman, Shui Lai and M.V. Klein
Solid State Com. 32, 51 (1981)
4. S. Pemozorov, A. Reznitskii, S. Verbin, G.O. Miller, R. Flogel and M. Nikiforova
Phys. Stat. Sol. (b), 113, 589 (1982)
5. V. Agekeyan, R. Bindenam, R. Schwabe, Yu. Stepanav and I. Streit
Phys. Stat. Sol. (b) 116, K 43 (1983)
6. M.D. Sturge, E. Cohen and R.A. Logan
Phys. Rev. B, 27, No. 4, 2362 (1983)
7. M.V. Klein, M.D. Sturge and E. Cohen
Phys. Rev. B, 25, No. 6, 4331 (1982)
8. Shui Lai and M.V. Klein
Phys. Rev. Letters, 44, No. 16, 1087 (1980)
9. Shui Lai and M.V. Klein
Phys. Rev. B, 29, No. 6, 3217 (1984)
10. L. Samuelson and M.E. Pistol
Solid State Com., 52, No. 9, 789 (1984)
11. E. Cohen and M.D. Sturge
Phys. Rev. B, 25, No. 6, 3828 (1982)
12. L. Samuelson, P. Onling, H. Titze and H.G. Grimmeiss
Journal de physique 12, C 5-323 (1982)

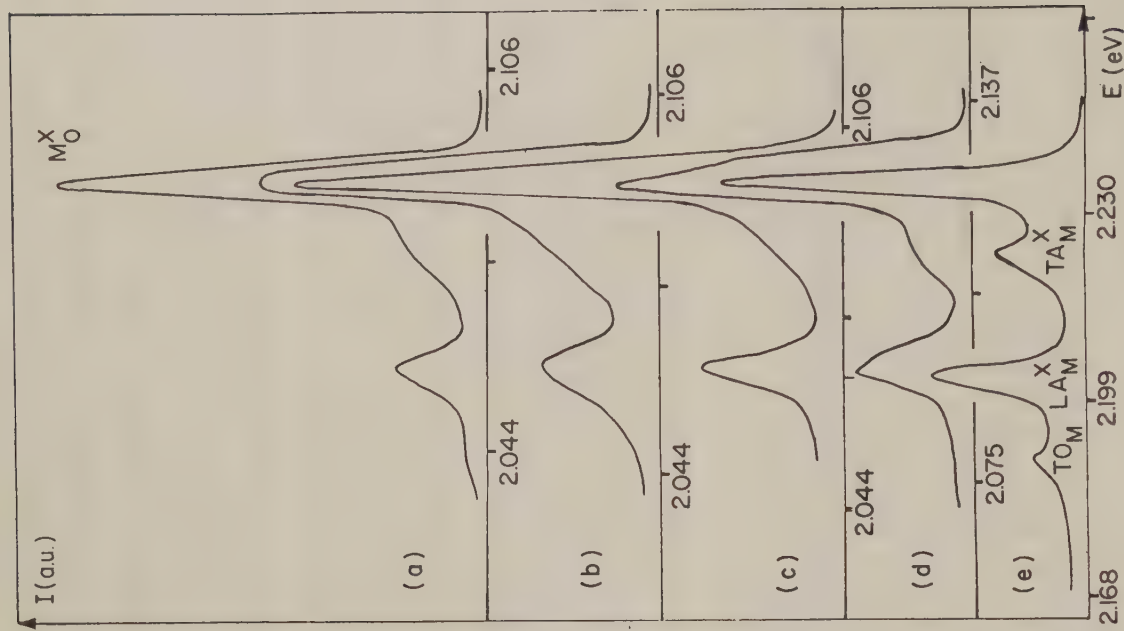


Fig. 1. Luminescence spectrum of $\text{GaAs}_{1-x}\text{P}_x$ at $T = 2\text{K}$ and for excitation

power $P = 40 \text{ mW/cm}^2$:

- a) $x = 0.51$, b) $x = 0.52$, c) $x = 0.56$, d) $x = 0.61$,
e) $x = 0.85$. TA_M^X , LA_M^X are phonon replicas of M_O^X .

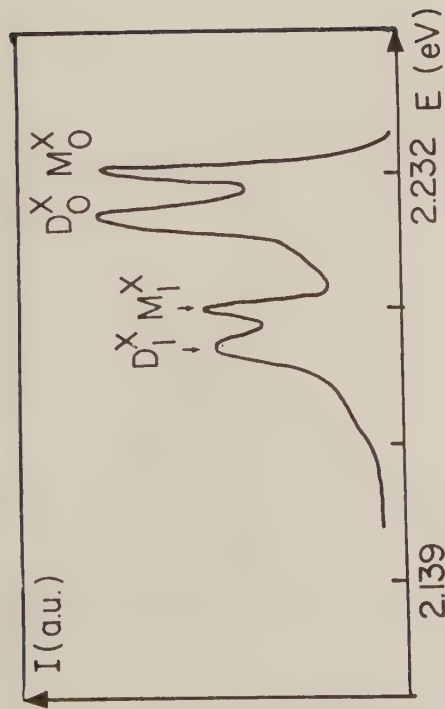


Fig. 2. Luminescence spectrum of $\text{GaAs}_{0.15}\text{P}_{0.85}$ at $T = 5\text{K}$ and for excitation power $P = 2.2\text{ W/cm}^2$. M_1^X and D_1^X are LA^X phonon replicas respectively of M_0^X and D_0^X (donor bound exciton).

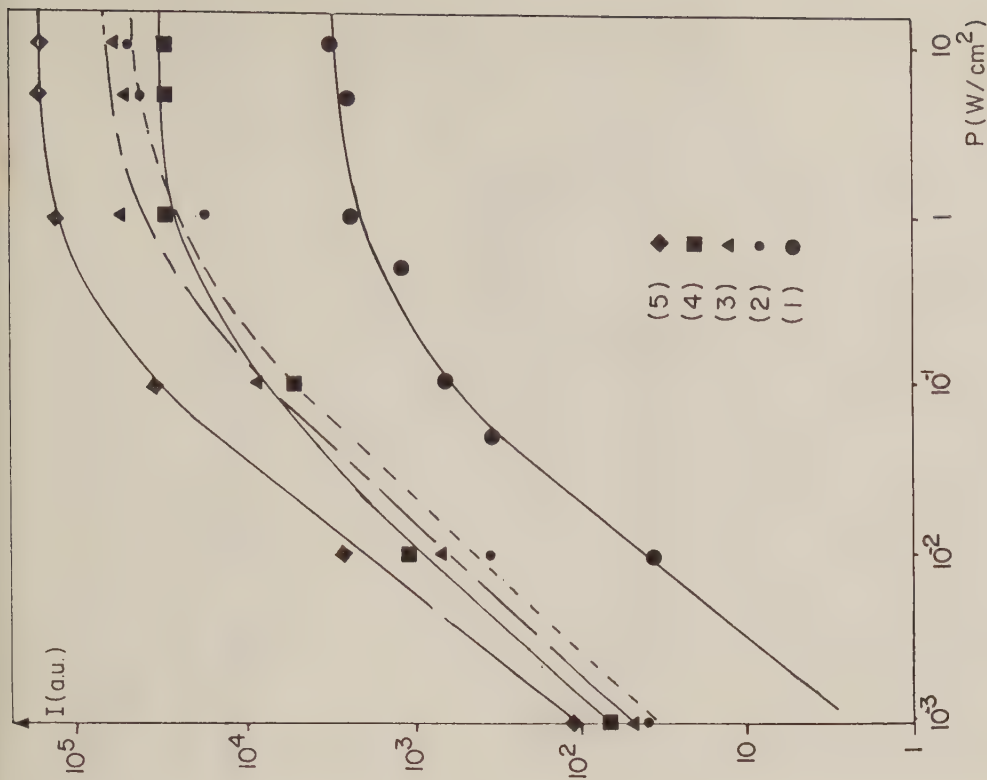


Fig. 3. Intensity of M_0^X as a function of excitation power P :

- 1) $x = 0.85$, 2) $x = 0.61$, 3) $x = 0.52$, 4) $x = 0.51$,
- 5) $x = 0.56$.

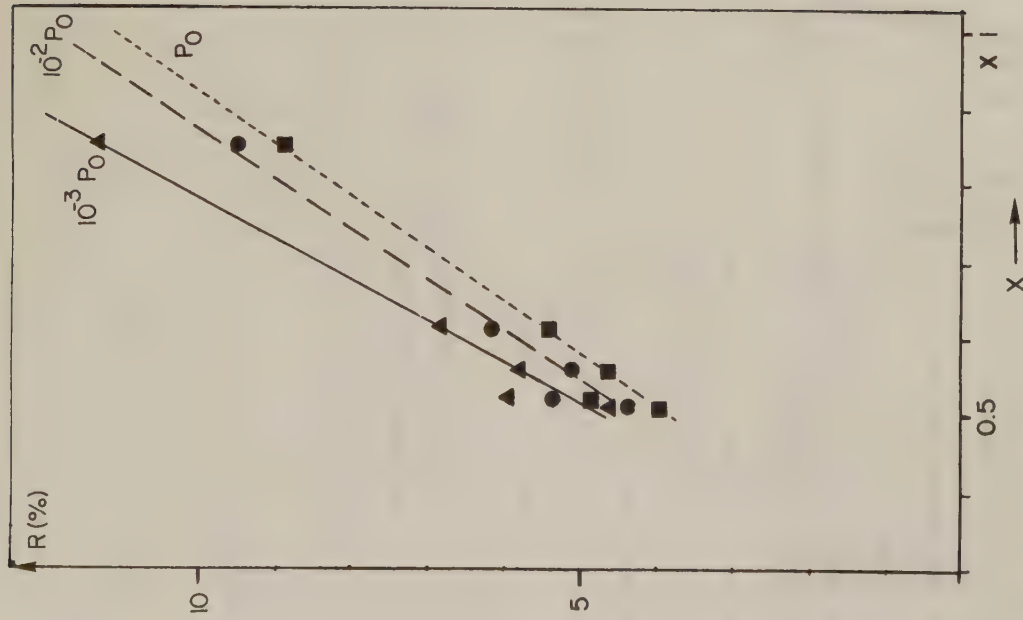


Fig. 4. Intensity ratio $R = \frac{I_{M_1}^x}{I_{M_0}^x}$ as a function of composition x , for different excitation power: a) $10^{-3}P_O$, b) $10^{-2}P_O$, c) $P_O = 10 \text{ W/cm}^2$, in $\text{GaAs}_{1-x}\text{P}_x$ alloys.

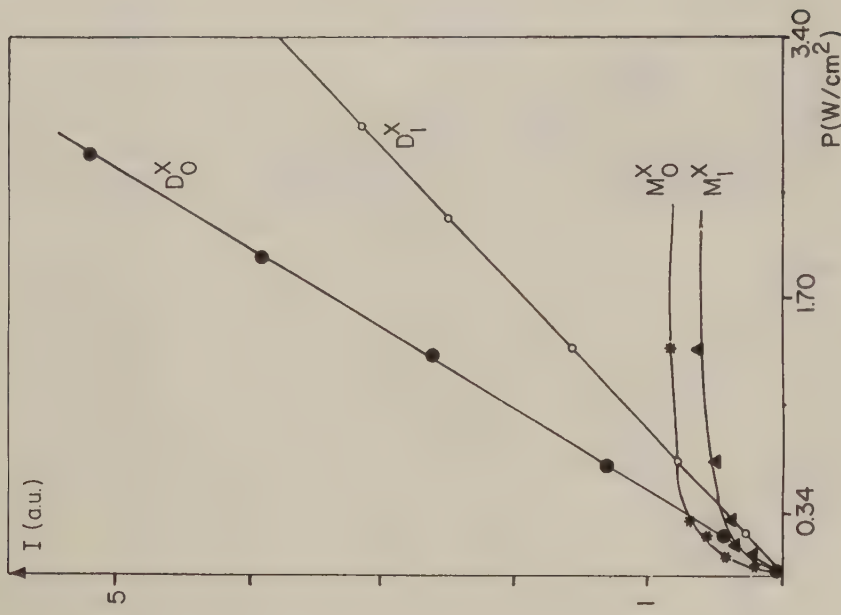


Fig. 5. M_0^x , M_1^x , D_0^x and D_1^x intensities as a function of excitation power P , at $T = 5K$, in $\text{GaAs}_{0.15}\text{P}_{0.85}$.

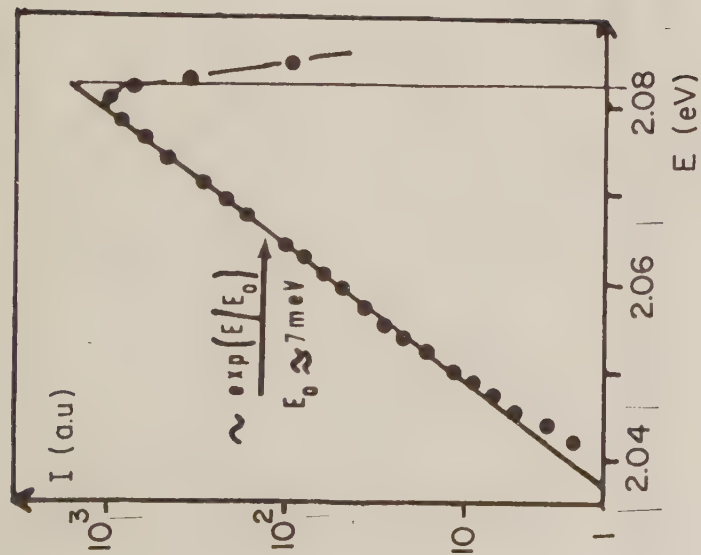


Fig. 6. Luminescence spectrum of M_0^X plotted semilogarithmically displaying the exponential dependence of the low energy tail.

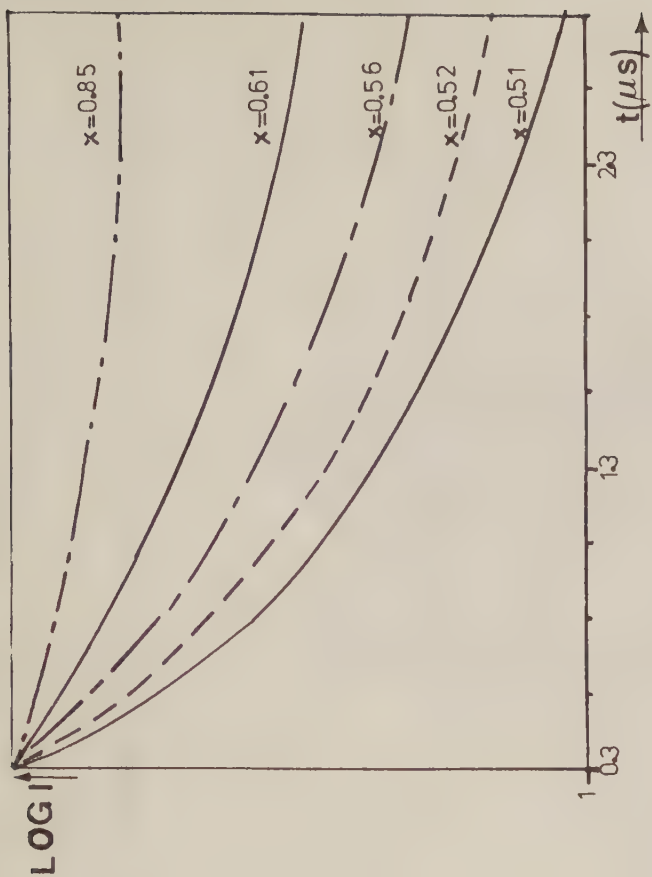


Fig. 7. Intensity time dependence of M_0^X peak in $\text{GaAs}_{1-x}\text{P}_x$ alloys, at $T = 2\text{K}$ and for $P = 10 \text{ mW/cm}^2$.

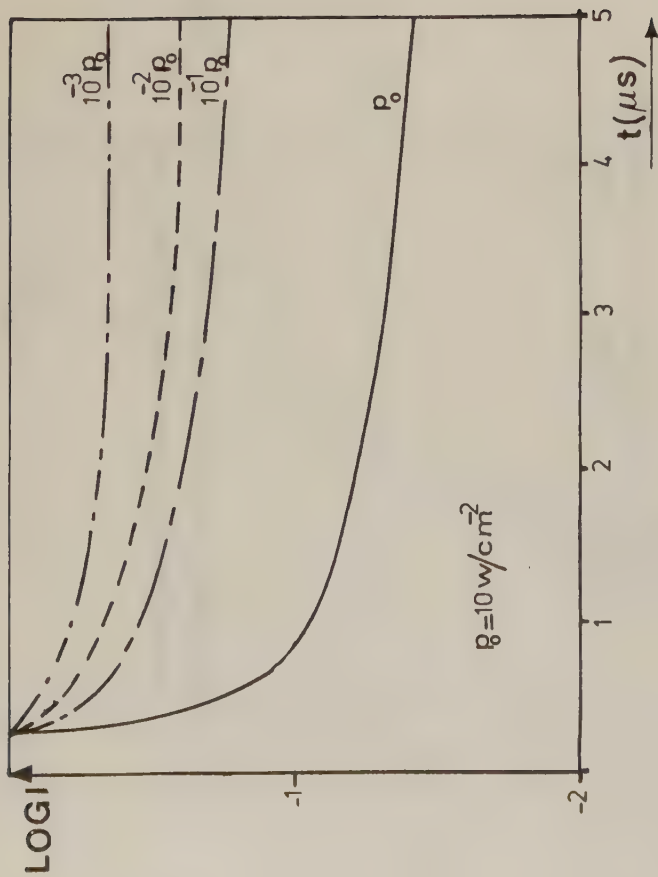


Fig. 8. Intensity time dependence of M_0^X peak in $\text{GaAs}_{0.15}\text{P}_{0.85}$ at $T = 2\text{K}$, for different excitation powers; $P_0 = 10 \text{ W/cm}^2$.

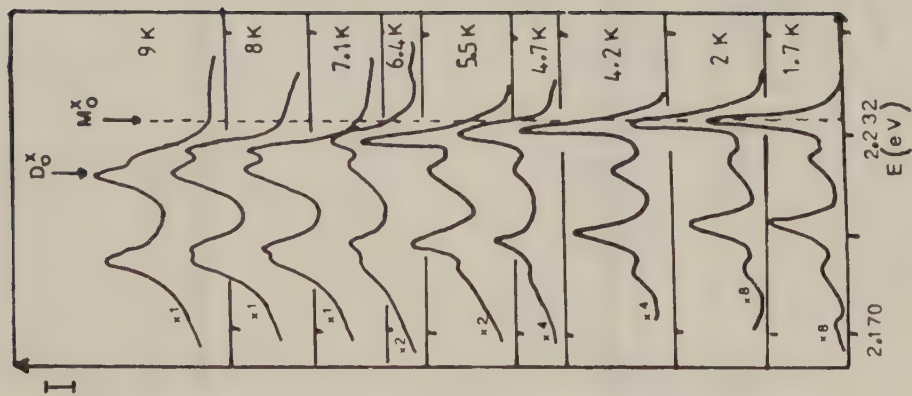


Fig. 9. Luminescence spectra of $\text{GaAs}_{0.15}\text{P}_{0.85}$ at different temperatures T , for $P = 0.5 \text{ W/cm}^2$.

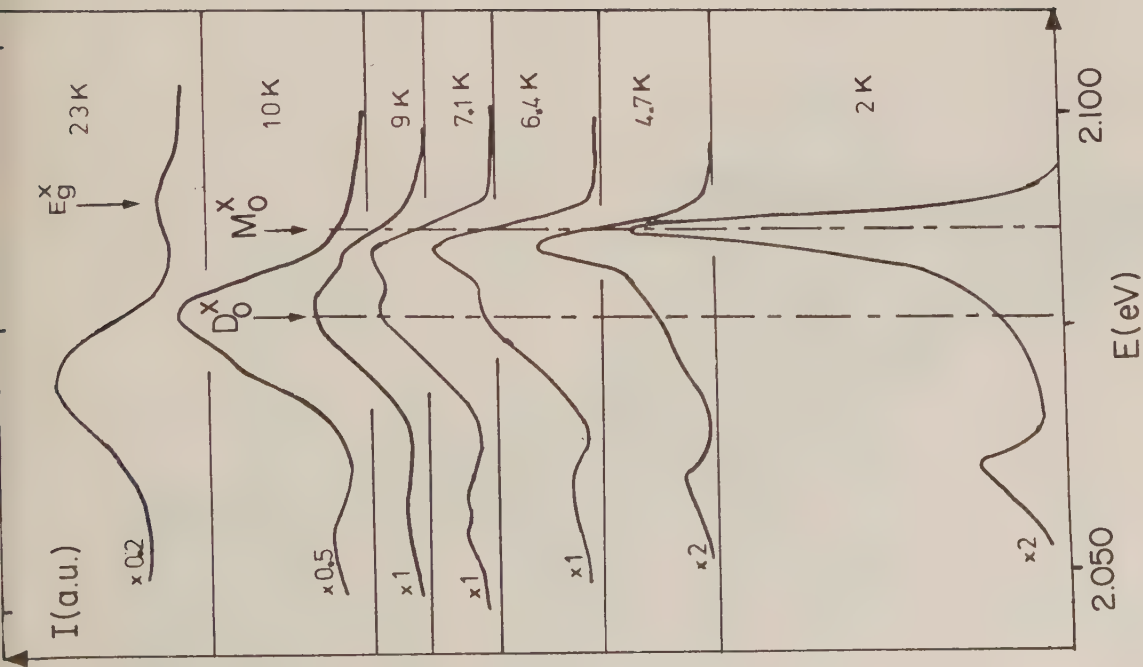


Fig. 10. Luminescence spectra of $\text{GaAs}_{0.49}\text{P}_{0.51}$ at different temperatures T , for $P = 0.5 \text{ W/cm}^2$.

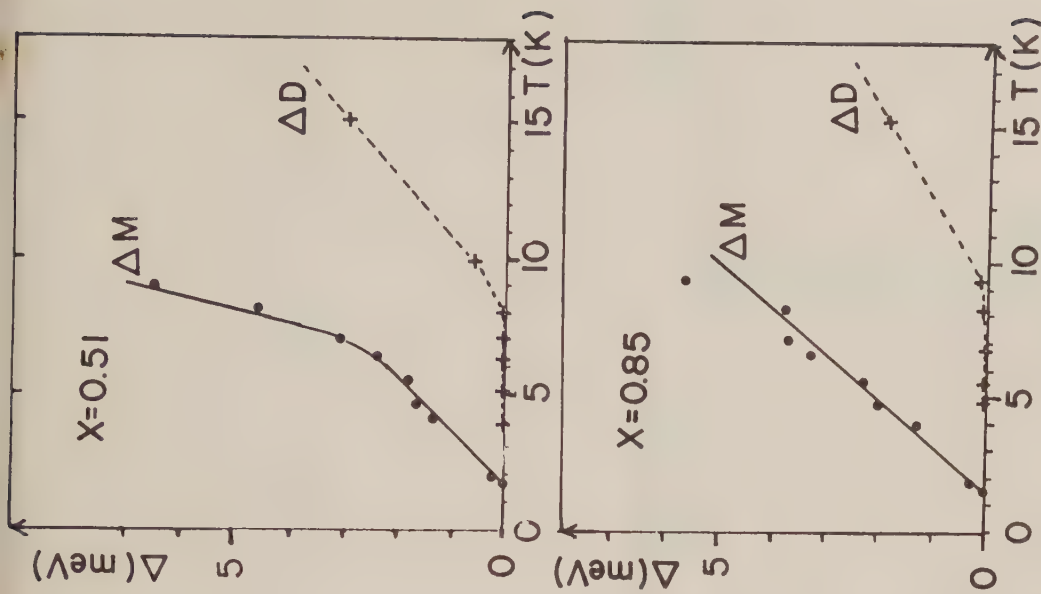


Fig. 11. Energy shift of M_0^x and D_0^x peaks as a function of temperatures T , in $\text{GaAs}_{1-x}\text{P}_x$.

$$\Delta M = E_{M_0^x}(T = 1.7\text{K}) - E_{M_0^x}(T) \text{ and}$$

$$\Delta D = E_{D_0^x}(T = 1.7\text{K}) - E_{D_0^x}(T)$$

a) $x = 0.51$, b) $x = 0.85$.

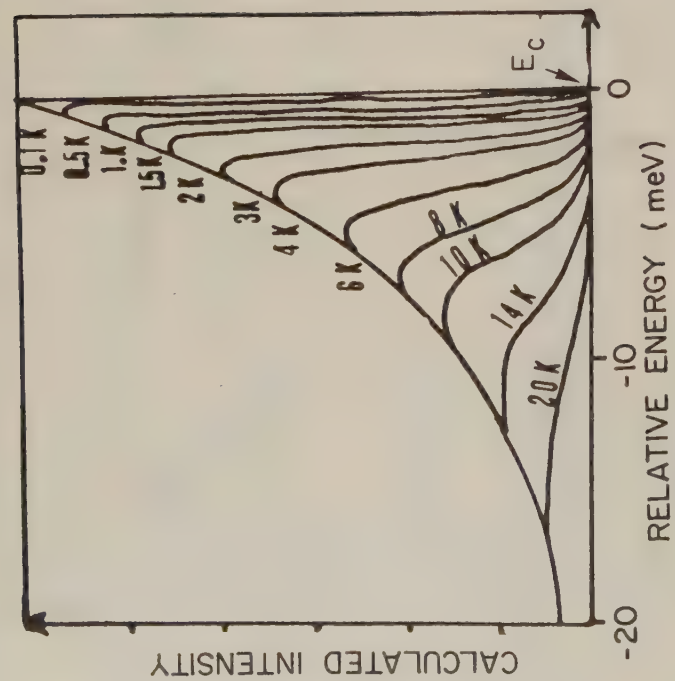


Fig. 12. The calculated lineshape of M_0^X at different temperatures. E_c is the energy of the high energy cut-off of M_0^X .

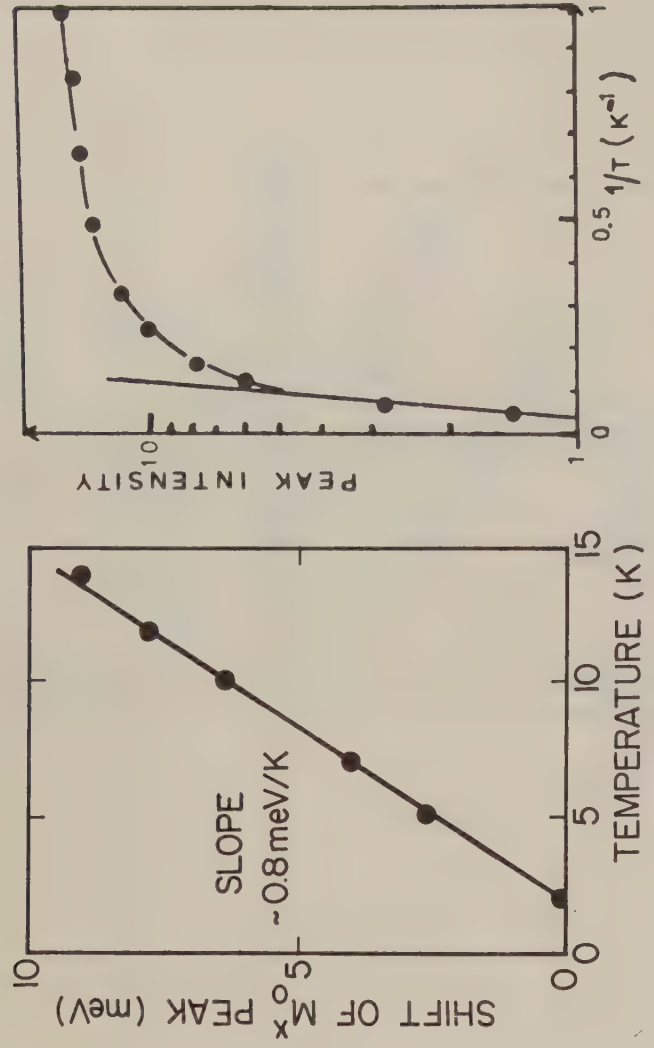


Fig. 13. a) Calculated shift of the M_0^X peak as a function of temperature.
 b) Calculated temperature quenching of the M_0^X -line giving an apparent activation energy of 3 meV.

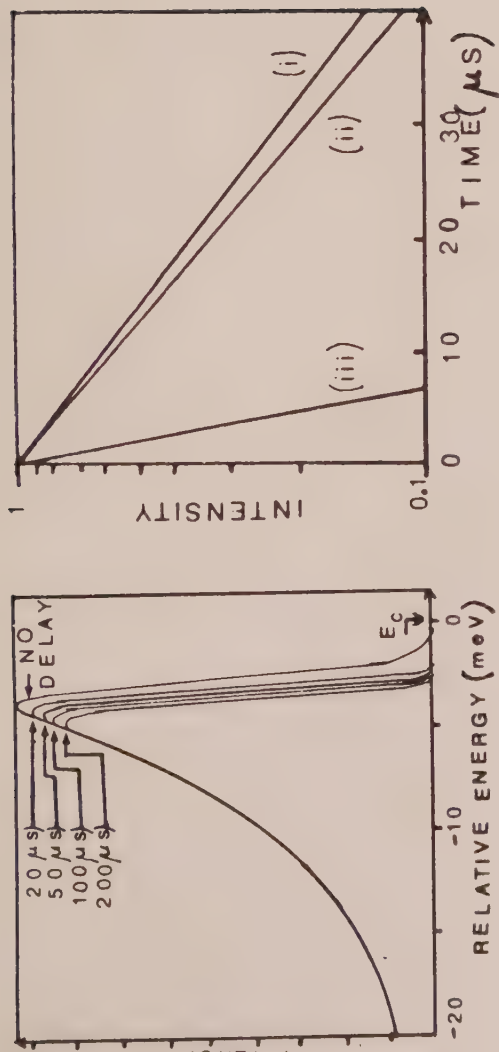


Fig. 14. a) Calculated lineshape of M_0^X at different delay times. The low-energy tail has been normalized to the same intensity in order to display the different decay times at different portions of the line.

b) Calculated intensity of (i) 1.4 meV towards the low-energy side from the peak, (ii) on the peak and (iii) 1.4 meV towards the high energy side from the peak, plotted logarithmically vs. time.

Cu diffusion in ZnTe in the temperature range 300-500°C gives rise to a neutral (isoelectronic) complex, which has been studied in this work via its bound exciton spectra at low temperatures. The bound exciton has a peculiar electronic structure with two electronic lines at 2.260 eV and 2.261 eV, respectively. The low energy line has a low oscillator strength, and is only strong in photoluminescence at low temperatures when favored by thermalization. In absorption only the electronic line at higher energy is seen. The two lines have quite different phonon coupling. Surprisingly enough they behave exactly the same in Zeeman measurements up to 10 T, indicating a similar electronic structure for both lines. An electronic excited state is observed at 2.363 eV, believed to be associated with $m_j = 1/2$ hole states, while the Zeeman data for the lower bound exciton lines are consistent with $m_j = 3/2$ holes. The peculiar doubling of the electronic structure is most naturally explained in terms of dynamic tunneling of an interstitial impurity atom around the main trigonal axis of the complex. An identity of the defect as a $\text{Cu}_{\text{Ga}}\text{-Cu}_{\text{I}}$ pair is suggested.

1. Introduction

Complex defects in semiconductors are of great technical importance, not least since they are often present in rather large concentrations as contaminants in the material from the growth and processing. Very few complex defects in semiconductors have been definitely identified, some well-known cases exist in GaP [1-3] and Si [4-6]. A similar situation is found with direct

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bandgap materials, where very little work has been published on complex defects [7-9]. Cu-diffusion in ZnTe produces a large number of complex defects [10-13]. ZnTe:Cu therefore presents an excellent playground for basic studies of complex defects in semiconductors, as summarized in a separate paper [13].

In this work we concentrate on one particular complex defect induced by a one-step Cu-diffusion at rather low temperatures, 300-500°C. This defect is neutral (isoelectronic) and binds an electron-hole pair (bound exciton) rather tightly at low temperature, producing two electronic lines at 2.2602 eV (B-line) and 2.2613 eV (A-line) respectively, in photoluminescence spectra. The lowest energy line has a low oscillator strength and is hardly detectable in absorption spectra. Zeeman data in transmission prove that the center is neutral (isoelectronic), since no thermalization between the Zeeman-split spectral components is observed in this case. The angular dependence of the Zeeman spectrum reveals a defect with basically trigonal symmetry.

The most surprising and interesting part of the electronic structure of this bound exciton is the fact that the two electronic states appear to have exactly the same magnetooptical behaviour. This is normally not observed, and is only conventionally explained in terms of two magnetically equivalent BE states, but associated with different vibrational states. We show that a dynamic tunneling for an interstitial impurity atom between different sites slightly off the trigonal axis of the defect could provide the proper origin of these two BE states.

At higher temperatures the B-line disappears, since thermalization into the higher energy state of much higher oscillator strength becomes important.

The phonon coupling spectrum of this center is rich in structure for the stronger A-line. The low energy B-line has a different and weaker phonon coupling than the A-line indicating that the corresponding bound exciton states have different symmetry. A strong excited state is also seen in dye-laser excited excitation spectra at 2.363 eV. This BE state is believed to be associated with an excited hole state configuration.

The Zeeman data indicate that the lowest energy BE states are derived from $m_j = 3/2$ hole states of the valence band top, i.e. the defect experiences an overall tensional axial stress field. The instability of the defect observed even at room temperature storage indicates that an interstitial is part of the defect. The simplest model for a trigonal neutral (isoelectronic) Cu-related defect is a $\text{Cu}_{\text{Zn}}\text{-Cu}_{\text{I}}$ pair. Due to the small size of the Cu_{I} atom this defect could still cause a tensional axial field.

In Sec. II below we describe the procedure for preparation of the samples and also the experimental techniques for optical spectroscopy. Sec. III deals with photoluminescence spectra and the related electronic structure of the bound exciton. Similar information from transmission data and photoluminescence excitation spectra (PLE) are also included. Sec. IV is concentrated on the details of the phonon coupling, which gives a rich structure within the one-phonon range. Unfortunately this

phonon spectrum is only partly understood in terms of possible defect-related vibration modes.

In Sec. V magnetooptical Zeeman data are presented, for both transmission and photoluminescence. These data were measured at fields up to 10T, and they provide the most important background for the detailed understanding of the electronic structure of the bound exciton. A model Hamiltonian gives a very good fit to experimental data for the Zeeman splitting of both electronic lines.

Sec. VI contains a discussion on the electronic and geometrical structure of this Cu-related neutral (isoelectronic) defect. The suggested identification of the defect is discussed in terms of available experimental data.

II. Sample Preparation and Experimental Procedure

II.1 Cu-doping in ZnTe

The starting material used for this investigation was nominally undoped bulk ZnTe prepared by B. Schaub, LETI, Grenoble by a modified Bridgman technique from Te solution. This material had a low electrically active doping level, in the 10^{14}cm^{-3} range. Single crystalline samples with a typical size $5\times 5\times 1\text{ mm}^3$ were cut from larger polycrystalline slices. The samples were polished and etched (2% Bromine-methanol solution, 3 min), prior to evaporating a thin Cu layer on the surface in high vacuum ($\approx 10^{-6}\text{torr}$). This Cu-layer served as the diffusion source in the subsequent diffusion process, which was typically performed in a single step using an open furnace

with N_2 -flow system at controlled temperatures. For this particular work diffusion temperatures, T_d , of 300-500°C were optimal and a typical diffusion time was one hour. A slow cool down procedure in the furnace was always used, to avoid the severe dislocation formation usually present with rapid cooling. After the diffusion the samples were polished again to remove the Cu diffusion source, and the above etching procedure was repeated. This Cu-diffusion procedure was sufficient to produce a large number of Cu-related complex defects in the material [13], and the temperature range 300°C $< T_d < 500^\circ\text{C}$ is particularly useful to give a suitable concentration of the defect giving rise to the 2.261 eV BE spectrum discussed here. The thermal stability of the defect was rather poor, however, and even a room temperature storage in darkness for a month was usually sufficient to render the BE spectrum undetectable, indicating that the defect had decomposed.

II.2 Optical measurements

Several different optical experiments were included in the present investigation, each requiring specific equipment. For the transmission experiments a simple set up was used with an ordinary tungsten lamp as excitation source, and the light transmitted through the He-cooled sample was detected via a 0.75 m Jarrell Ash double monochromator. In the photoluminescence experiments the same monochromator was used, with an Ar^+ laser or a tunable dye-laser as excitation source. For photoluminescence excitation (PLE) spectra the tunable dye-laser was always used, with a stepping motor for continuous scanning of the wavelength. Sample temperatures could be

controlled continuously between 1.8K and room temperature.

The magnetooptical data were obtained with a 10T superconducting magnet at the Max Planck Hochfeld Magnetlabor in Grenoble. For this work only the Voigt configuration was used, and both transmission and photoluminescence experiments were performed. A Jobin Yvon 1500 high resolution double monochromator was used on the detection side.

III. Optical Spectra for the 2.261 eV Bound Exciton

The photoluminescence (PL) spectrum at 2K for the 2.261 eV Cu-related BE with 5145Å Ar⁺ laser excitation is shown in fig 1. Two electronic lines are present for this bound exciton, line B at 2.260 eV and line A at 2.261 eV. The weaker B-line has ~20% of the intensity of higher energy A line in PL at 2K.

When the temperature is raised the low energy line B is gradually quenched, as obvious from fig 2. This is interpreted as a thermal excitation from the lower electronic state to the upper one at the higher temperature. The two lines A and B appear with a very similar intensity ratio at a specific temperature in a large number of samples studied, which would hardly be expected if they were connected with two different defects.

The identification of the weaker B line as an electronic line and not a low energetic quasilocalized phonon related to the A line is based on the following observations. The B line is very sharp, of the same linewidth as the electronic A line, which is hardly expected for a quasilocalized phonon mode, even though

the lattice phonon density of states gives a quite low continuum background at these low energies. Also, the corresponding mode is absent on the high energy side of the A line in absorption (fig 3). Instead, a very weak feature is actually seen in excitation spectra (fig 4 below), at the expected position 2.260 eV, if the B line is of electronic origin. Consequently we consider the B line as being an electronic line in what follows.

The total emission spectrum in fig 1 shows a rich phonon sideband dominated by a low energy quasilocalized phonon $\bar{\Gamma}_1$, of ~5.3 meV, and a number of replicas in the optical range of the one-phonon spectrum. The Lo^{Γ} replica has the strongest coupling strength among the phonons, and is observed with the same coupling constant for both electronic lines. Otherwise the phonon wing is totally derived from the higher energy A line, and the B line phonon coupling is not obvious, except for the above mentioned Lo^{Γ} replica. More details of the phonon coupling to this BE is given in Sec IV.

The optical transmission spectrum at 2K related to this BE is shown in fig 3. The most striking observation from this spectrum is that the low energy electronic B line is very weak, while the A line at 2.261 eV is seen strongly. This is obviously due to a very weak oscillator strength of the B line, consistent with the observed thermalization in the PL spectra above (fig 2).

A more detailed picture of the phonon spectrum associated with this BE in absorption is revealed by dye-laser excited PLE

spectra, as shown in fig 4. A rich phonon-assisted wing corresponding to what is observed on the low energy side of the electronic lines in PL emission (fig 1) is observed in fig. 4. The phonon energies are listed in table 1, and compared to the corresponding observations in PL spectra (fig 1).

At higher photon energies these PLE spectra show a very strong peak C at ≈ 2.3633 eV (fig 5), which is interpreted as an excited electronic state of the exciton. The possible origin of this state is discussed below in Sec. V. With selective dye-laser excitation resonant with this line the characteristic BE luminescence spectrum shown in fig 1 is produced strongly. This further supports the assignment of the 2.3633 eV C line as an excited electronic state to this exciton. In fact the alternative possibility that this line would not belong to the same defect, but rather be another BE line associated with a different center, would imply that this line would occur in luminescence as well, which is not seen. No PL lines are observed close to this energy in these samples.

IV. Phonon Coupling in the Bound Exciton Spectrum

The spectral information on the phonon coupling to this BE system is essentially contained in figs 2 and 4, and in Table 1. The phonon coupling is rather strong in this case. The strength can be expressed by $S_{\text{tot}} = S_{\lambda} + S$, where S_{λ} represents the coupling strength (= ratio between intensity of one-phonon replica and the corresponding electronic transition line) of discrete phonons and S represents the strength of the coupling to the continuous phonon band, (14). An analysis of

the spectrum in fig 1 yields the approximate values $S_{\text{tot}} = 2$, $\sum_{\lambda} S_{\lambda} = 1$ and $S = S_{\text{tot}} - \sum_{\lambda} S_{\lambda} = 1$. The approximate values of S_{λ} for the different discrete phonons λ are found in Table 1. As mentioned above replicas are only observed to the A line, except for the weak LO^{Γ} line associated with the low energy B line. The contribution from the continuous band in the one-phonon range from the B-line cannot be established from the spectra. It is therefore supposed in the above analysis that the background is due to the A-line alone.

The variety of phonon modes observed in the spectrum correspond to different local vibrations at the defect in addition to the lattice modes. The theoretical modelling of complex defect vibration modes has been discussed in the literature for substitutional complexes [15-17], but no detailed work seems to be present for such complexes involving interstitial species. As discussed in more detail in Sec. VI, we believe this complex contains an interstitial Cu_i , in fact a defect identity as $\text{Cu}_{\text{Zn}} - \text{Cu}_i$ in a trigonal $\langle 111 \rangle$ orientation is suggested.

From previous studies such defects are found to produce low energy quasilocalized modes, probably from the motion of the interstitial atom [7-9, 14, 18-20]. Several such modes are seen when more than one interstitial is involved in neutral (isoelectronic) complexes, as in the III-V materials [14, 18-20]. One low energy mode has been found to dominate for analogous defects in ZnSe:Ag [9] and ZnTe:Ag [7], in both cases for neutral defect complexes tentatively identified as a $\text{Ag}_{\text{Zn}} - \text{Ag}_i$ pair. This is similar to the spectrum in fig 1, where the dominating low energy mode at 5,3 meV therefore supports the idea of a $\text{Cu}_{\text{Zn}} - \text{Cu}_i$ neutral (isoelectronic)

complex as the identity of the center. Additional sharp modes occur resonant with the optical part of the ZnTe one-phonon spectrum, as shown in fig 1, but the LO^r replica dominates by far, as usual in such spectra. No strong modes are observed at the gap energies (i.e. the gap between acoustic and optical phonon modes in ZnTe) [13,21]. This is contrary to the observations for other complex defects in ZnTe, where sharp "gap modes" are usually observed [13].

V. Magnetooptical Zeeman Data for the 2.261 eV Bound

Exciton

As mentioned above the Zeeman measurements were performed both in transmission and photoluminescence. A typical set of transmission data for the 2.261 eV BE is shown in fig 6, for magnetic fields varying from 1 to 10T. Only the electronic A-line is seen, as mentioned above, while the B-line has a much lower oscillator strength. The spectrum in fig 6 is obtained for an arbitrary crystal direction versus the magnetic field, and shows a complicated splitting with the magnetic field. An important point is the complete absence of thermalization in the Zeeman spectrum, which means that the full spectrum is observed at all fields. This proves beyond doubt that the BE is associated with a neutral (isoelectronic) defect and not an acceptor (or donor), since in the latter case a splitting of the ground state of the BE would occur leading to thermalization in transmission. A neutral (isoelectronic) center has no particle in the ground state of the BE transition, hence no thermalization can occur in absorption.

Another important result from fig 6 is the sizeable diamagnetic shift observed for the center of gravity of the Zeeman split BE spectrum. The shift amounts to $\approx 5.5 \times 10^{-3} \text{ meV/T}^2$, smaller than but comparable to the case of shallow donor electrons in ZnTe [22]. This verifies that the electron is rather loosely bound like a shallow donor electron by the positive charge of the center when it has already captured a hole. The defect is expected to be predominantly hole-attractive due to the Cu_{zn} central cell, which means that the hole is expected to be captured first in a rather localized state. This is the conventional so called HTL model [23]. The binding energies can be estimated to be $\approx 120 \text{ meV}$ for the hole and $15\text{--}16 \text{ meV}$ for the electron.

Transmission spectra were also recorded in the Voigt configuration at 10T, for different polarizations, as shown in fig 7. If these spectra are taken with the (100) direction along the magnetic field $\bar{B}$, no difference in the spectra is observed between σ and π polarization. At an arbitrary angle with this symmetry axis (with $\bar{B}$ along (100)) all trigonal defects are in fact equivalent), strong differences in polarization behaviour are observed for different Zeeman split spectral lines.

In fig 8 is shown the photoluminescence spectrum of the 2.26 eV BE lines as a function of magnetic field up to 10T. Both lines A and B are now detectable, and a striking observation is that they appear to behave exactly in the same way as far as Zeeman splitting is concerned. This is further confirmed in the

angular dependence of this Zeeman spectrum, shown in fig 9 for a magnetic field of 10T. Apart from demonstrating the equivalence of line A and B in the Zeeman spectrum, this synopsis also clearly establishes the defect as one with a $\langle 111 \rangle$ oriented trigonal symmetry axis. This is a very important result, since it basically suggests the previously mentioned model of a $\text{Cu}_{2n} - \text{Cu}_j$ trigonal defect as the identity of this center. The explanation for the existence of two different electronic lines associated with this defect, with the same magnetooptical behaviour for both, will be given below in Sec. VI in terms of the existence of two different vibrational states for the exciton associated with a Cu_j which is slightly distorted off the trigonal $\langle 111 \rangle$ main axis of the defect.

The detailed evaluation of magnetooptical Zeeman data is performed with the aid of a general model Hamiltonian [24-27]

$$H = H_{\text{ex}} + H_{\text{CCF}} + H_{\text{TCF}} + H_{\text{LZ}} + H_{\text{QZ}}$$

where $H_{\text{ex}} = -a\vec{J} \cdot \vec{S}$ denotes the bound electron-hole exchange interaction, $H_{\text{CCF}} = -b(J_{\text{x x}}^3 + J_{\text{y y}}^3 + J_{\text{z z}}^3)$ gives the effect of the cubic crystal field, $H_{\text{TCF}} = -D[J_{\text{z}}^2 - \frac{1}{3}J(J+1)]$ describes the trigonal crystal field term, while the two last terms are the Zeeman terms induced by the magnetic field: the linear interaction term

$$H_{\text{LZ}} = \mu_{\text{B}}[g_{\text{e}}\vec{S} \cdot \vec{H} + K\vec{J} \cdot \vec{H} + L(J_{\text{x x}}^3 + J_{\text{y y}}^3 + J_{\text{z z}}^3)]$$

and the quadratic term

$$H_{\text{QZ}} = c_1 H^2 + c_2 (\vec{J} \cdot \vec{H})^2 + c_3 (H_{\text{x y}} H_{\text{x y}} \{J_{\text{x y}}^J\} + H_{\text{y z}} H_{\text{y z}} \{J_{\text{y z}}^J\} + H_{\text{z x}} H_{\text{z x}} \{J_{\text{z x}}^J\}).$$

Here $\vec{J}$ denotes the total "spin" of the bound hole, $\vec{S}$ the bound electron spin, μ_{B} is the Bohr magneton, x, y, z refer to the usual cubic axes, and z to the threefold trigonal axis. $\{J_{\text{x y}}^J\}$ stands for the commutator $\frac{1}{2}(J_{\text{x y}}^J + J_{\text{y x}}^J)$ etc.

The trigonal crystal field is considered the main perturbation of the bound hole states, meaning that the Γ_{g} quadruplet of hole states in tetrahedral symmetry can approximately be described as split into two independent Kramers doublets $|3/2, \pm 3/2\rangle$ and $|3/2, \pm 1/2\rangle$ in the usual $|J, m_j\rangle$ notation [28]. For a tensonal crystal field the lowest energy bound hole state would be the $m_{\text{h}} = m_j = \pm 3/2$ state, which combined with the $m_{\text{e}} = \pm 1/2$ electron forms the observed bound exciton state. The quantization axis is naturally the trigonal defect axis.

The resulting fit for the experimental Zeeman data to the above Hamiltonian with these assumptions are shown in fig 9 and 10. Here the two lines A and B at zero field are treated as independent equivalent electronic states of the bound exciton, which will be further justified below under Sec. VI:1. A second electronic line associated with each of the A and B lines is observable for fields above $\approx 1\text{T}$. This second line, shifted towards lower energy, which apparently is forbidden at $H=0\text{T}$, is identified as the $|m_{\text{h}}=\pm 3/2, m_{\text{e}}=\pm 1/2\rangle$ bound exciton state. The higher energy lines A and B (observable at zero field)

correspond to the $|m_h = \pm 3/2, |m_e = \pm 1/2\rangle$ states in the $|m_h, m_e\rangle$ notation. The 2,363eV excited state is assumed to be formed from a $|j=3/2, m_h \pm 1/2\rangle$ hole state which combined with an electron state gives rise to a $|m_e = \pm 1/2, m_h = \pm 1/2\rangle$. This state is believed to have a strong oscillator strength according to the selection rules for transitions from the ground state of the defect.

The parameters giving the best fit to the angular dependence data in fig 9 and the fan diagram in fig 10 are listed in Table 2. An electron-hole exchange splitting parameter, $a = 0,22$ meV is evaluated, together with a trigonal splitting term $D = 51,1$ meV. More importantly, the magnetooptical parameters $g_e = -0,40$, $K = 0,70$, $L = 0,17$ and $c_1 = 5,5 \cdot 10^{-3} \text{ meV/T}^2$ are obtained for the 2.261eV state. This g_e value is typical for shallow electron states in ZnTe [29]. Likewise the K-value is typical for $m_j = \pm 3/2$ holes in ZnTe. The parameters for the lower 2.260 eV electronic B-state are the same within the errors involved in the fitting procedure.

It should be reminded that the experimental accuracy of the wavelength reading between spectra taken at different magnetic fields is of the same order as the observed small deviations from the computed model behaviour in figs 9 and 10. Further the observed scatter in data close to $\langle 110 \rangle$ in fig 9 is easily obtained with a slight misorientation of the sample a couple of degrees. The fit is therefore to be regarded as quite satisfactory, and gives strong support to the basic assumptions in the model used.

VI. Discussion

VI.1 Electronic structure of the bound exciton

The experimental data on the 2.261 eV BE spectra displayed in Sec. III-V above have established beyond doubt that the defect responsible for binding this particular BE is basically a trigonal neutral (isoelectronic) complex. In addition the BE has the very unusual property that it contains two electronic states with identical magnetooptical properties, as far as can be resolved at fields up to 10T. The Zeeman data further reveals an electron-hole exchange splitting of about ≈ 0.2 meV for each of these lines, an anisotropic hole g-value characteristic of $m_h \approx 3/2$ for both lines, and also in both cases an electron g-value of $g_e \approx -0.40$ typical for a shallow donor-like electron in both BE states. This picture is also consistent with the observed diamagnetic quadratic shift rate of the BE as being $\approx 5,5 \cdot 10^{-3} \text{ meV/T}^2$ for both these lines. The only apparent difference between the lines is therefore the oscillator strength, which is much weaker for the low energy line. This difference is at least two orders of magnitude as inferred from the data in figs 3 and 4 above.

As already mentioned, it has been ruled out from the statistics of a large number of samples studied that both these lines are in fact associated with different defects. If not one would expect to see variations in relative intensity of these two lines between samples prepared under different diffusion conditions. No such variations have been observed. Further it seems very improbable that the two lines could be due to an

isotope splitting caused by Cu^{63} and Cu^{65} at equivalent sites in a complex. The observed "splitting" is here at least an order of magnitude larger than expected for isotope splittings of electronic BE lines in semiconductors [30]. Further the oscillator strength would be expected to occur in a ratio similar to the natural Cu isotope ratio $\approx 1:4$, which is clearly not the case.

There seems to be no possibility to imagine two different hole states with slightly different binding energies in this case. We may assume that the hole is primarily bound to the defect by virtue of the rather strongly hole-attractive pseudopotential associated with Cu_{Zn} . In axial symmetry the degeneracy of the hole-states is split, in this case with a tensional local strain field in a way to lower the energy of $m_h = \pm 3/2$ hole states (approximate notation strictly valid only in tetrahedral symmetry [28]), while the $m_h = \pm 1/2$ hole states are higher in energy (fig 11). Since the two hole states have quite different anisotropy for the g-value, a weak such trigonal splitting causing the two electronic lines can be ruled out from our Zeeman data (fig 9). Consequently the source of two electronic lines will have to be searched for in the bound electron state, i.e. the secondary particle loosely bound to the defect.

Indeed for the normal shallow donor states on substitutional tetrahedral sites in ZnTe , the direct bandgap with a lowest Γ_6 conduction band can only produce one bound electron state (disregarding orbitally excited states). In the case of a complex defect with an interstitial atom as part of the complex the situation may be different. Along the trigonal axis there

are two different tetrahedral interstitial sites in the zinc-blende lattice, which are not electronically equivalent, since one of them has a Zn-like pseudopotential (electron-repulsive) while the other is Te-like and electron-attractive [31]. This means that an interstitial donor might have different binding energies and also a different symmetry of the bound electron wavefunction for these two cases. A trigonal defect made up of a Cu_{Zn} and an interstitial would then have exciton states of different binding energies if the interstitial had the choice of occupying any of these two interstitial sites. Since the bandgap at ZnTe is direct at Γ , both these effective mass like states would be of Γ_6 symmetry, however, The observation of drastically different oscillator strengths and phonon coupling for the A and B lines suggests that in fact these states should have different symmetry. The model of two interstitial sites along the trigonal axis is therefore not satisfactory.

An alternative model involves slight distortions of the Cu_i atom out from the trigonal axis of the defect, as schematically illustrated in fig. 12. Such a distortion could be caused by the rather high ionicity of ZnTe ($f_i \approx 0.6$ for ZnTe [32]). This means that Te atoms will have an excess negative charge, while the Zn atoms will tend to be more positive. This distribution of charges will tend to distort the positive Cu_i atom out from the trigonal axis, (fig. 12), in a similar way as previously observed for KCl:Li [33].

The effect on BE states of such distortions may be understood in the following model. It is assumed that the hole is mainly bound by the Cu_{Zn} pseudopotential (and the strain field),

and is not in the first approximation affected by slight distortions of the interstitial. The electron, on the other hand, is rather loosely bound, as evidence from the shallow donor-like g-value $g_e = -0.4$, and is therefore also not much affected by slight distortions of the interstitial. Consequently the electronic part of the BE wave function ψ_{ex}^{el} is approximately independent of the nuclear coordinates of the interstitial.

The existence of two different BE states to the same defect is therefore not explained by the electronic part ψ_{ex}^{el} , but rather a consequence of the nuclear vibrations of the interstitial, involving three equivalent positions around the trigonal axis (fig. 12). If the potential barrier is low, all three sites may be involved. Two different vibrational states of the BE

$|\psi_V^{BE}\rangle$ of A_1 and E symmetry respectively will be formed for the trigonal case. This will explain the occurrence of two BE lines, if there is only one vibrational state of symmetry A_1 , $\psi_V^G(A_1)$, in the crystal ground state, giving an appreciable

vibrational overlap. If the vibrational overlaps

$\langle \psi_V^{BE}(A_1) | \psi_V^G(A_1) \rangle$ and $\langle \psi_V^{BE}(E) | \psi_V^G(A_1) \rangle$ are quite different, as

expected, these two lines will have strongly different oscillator strengths. The L_1 phonon replica may correspond to a vibrationally excited state of the crystal ground state, where the vibration is of a dynamic tunneling type.

It should be pointed out that dynamic motion of a similar type between equivalent sites have been observed previously for complex donors involving Li as well as complex acceptors involving H in Ge [34,35]. A similar case is observed for a C-related complex in Si, where the C-atom is close to being bond-centered [36]. This is believed to be the first observation of dynamic motion of a rather heavy atom like Cu around a high symmetry axis of a defect.

VI.2 Defect identity

So far the model for the defect (fig 12) is shown to probably involve a Cu_{Zn} and in addition an interstitial atom on a trigonal axis. The identity of this interstitial is not known, but we argue the most probable choice is Cu_i . The main reason for this is the fact that the defect is produced under

equivalent Cu-diffusion conditions in both doped or nominally undoped material with residual net acceptor concentration of $< 10^{15} \text{ cm}^{-3}$. No correlation with impurities other than Cu

was therefore established, rather the defect is typically produced by only Cu diffusion into pure ZnTe. This is easily understood with a diffusion model involving Cu_i as a rapid interstitial diffuser, complexing with Cu_{Zn} at the diffusion temperature to form a neutral (isoelectronic) trigonal defect. The observed instability of this defect correlates well with the idea that the Cu_i is rather unstable in this complex, and may easily break away even at room temperature. Such an instability is also observed with a number of other complex defects in Cu-doped ZnTe, all believed to involve Cu_i interstitials [13].

In summary we tentatively identify the neutral (isoelectronic) complex studied in this work as a trigonal axial defect involving two Cu atoms, one Cu_{zn} and in addition a Cu_i. It is further suggested that the Cu_i is slightly distorted off the trigonal axis. Dynamic tunneling between three different such distorted sites around the trigonal axis may explain the additional bound electron state dominant at higher temperatures in BE PL spectra.

VII. Acknowledgement

We thank Dr. Robert McMurray for pointing out the behaviour displayed by tunneling acceptors and donors in Ge.

Table 1. A tabulation of observed phonon modes, their coupling strength and the type of mode.

Notation	Energy displacement		Coupling strength		Interpretation
	from the A line (meV)		S_{λ} in PL		
	PL	PLE			
L ₁	5.3	5.6	0.09		Quasilocalized mode
L ₂	10.6		0.08		"
L ₃	15.9	15.9	0.04		"
L ₄		18.7			Gap mode
L ₅		19.7			"
L ₆	21.5	21.6	0.02		Quasilocalized mode
L ₇	23.0		0.03		"
L ₈	23.8	23.8	0.02		"
L ₉	26.0		0.50		L ⁰ r

Table 2. A comparison of the parameters describing the Zeeman splitting of the Cu related defect.

Parameters	A-line	B-line
a	0.22 meV	0.20 meV
D	51.15 meV	51.6 meV
g _e	-0.40	-0.40
K	0.70	0.67
L	0.17	0.15
C ₁	$5.5 \cdot 10^{-3} \text{ meV/T}^2$	$5.3 \cdot 10^{-3} \text{ meV/T}^2$
b	0	0
C ₂	0	0
C ₃	0	0

References

1. T.N. Morgan, B. Welber and R.N. Bhargava, Phys. Rev. 166, 751 (1968).

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C.H. Henry, P.J. Dean and J.D. Cuthbert, Phys. Rev. 166, 754 (1968).

2. P.J. Cean, Phys. Rev. B4, 2596 (1971).

3. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, Phys., Rev. B 25, 7719 (1971).

4. L. Canham, G. Davies and E.C. Lightowlers, Physica 117-118 B, 119 (1983).

5. N Killoran, D.J. Dunstan, M.O. Henry, E.C. Lightowlers and B.C. Carenett, J. Phys. C 15, 6067 (1982).

6. D. Labrie, T. Timusk and M.W.L. Thewalt, Phys. Rev. Lett. 52 81 (1984).

7. B. Monemar, P.O. Holtz, H.P. Gislason, N. Magnea, Ch. Uihlein and P.L. Liu, manuscript Phys. Rev. B.

8. M.S. Skolnick, P.J. Dean, A.D.Pitt, Ch. Uihlein, H. Kvath, B. Deveand and E.J. Foulkes, J. Phys. C 16, 1967 (1983).

9. P.O. Holtz, B. Monemar and H.J. Lozykowski, manuscript Phys. Rev. B.
10. D. Bensahel, N. Magnea and M. Dupuy, Solid state Commun. 30, 467 (1979).
11. N. Magnea, D. Bensahel, J.L. Pautrat, K. Saminadayar and J.C. Pfister, Solid State Commun. 30, 259 (1979).
12. P.O. Holtz, B. Monemar, H.P. Gislason, Ch. Vihlein and P.L. Liu, manuscript Phys. Rev. B.
13. B. Monemar, P.O. Holtz, H.P. Gislason and N. Magnea, manuscript Phys. Rev. B.
14. H.P. Gislason, B. Monemar, P.O. Holtz, P.J. Dean and D.C. Herbert, J. Phys. C 15, 5467 (1982).
15. D.N. Talwar, M. Vandevyver and M. Zigone, J. Phys. C 13, 3775 (1980).
16. R.M. Feenstra, R.J. Hauenstein and T.C. McGill, Phys. Rev. B 28, 5793 (1983).
17. R.J. Hauenstein, T.C. McGill and R.M. Feenstra, Phys. Rev. B 29, 1858 (1984).
18. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, A. Kandaah and B.C. Carenett, Phys. Rev. B, 15 March 1985.
19. H.P. Gislason, B. Monemar, M.E. Pistol, P.J. Dean, D.C. Herbert, S. Depiuna, A. Kandaah and B.C. Cavenett, submitted Phys. Rev. B.
20. H.P. Gislason, B. Monemar, M.E. Pistol. A. Kandaah and B.C. Cavenett, submitted Phys. Rev. B.
21. N. Vagelatos, D. Wehe and J.S. King, J. Chem. Phys. 60, 3613 (1974).
22. P.J. Dean, H. Venghaus, J.C. Pfister, B. Schaub and J. Marine, J. Lumin. 16, 363 (1978).
23. J.J. Hopfield, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. 17, 312 (1966).
24. J.M. Luttinger, Phys. Rev. 102, 1030 (1956).
25. A. Abragam and B. Bleaney in Pramagnetic Resonance in Transition Ions (Clarendon, Oxford 1970).
26. K. Cho, S. Suga, W. Dreybrodt and F. Willmann, Phys. Rev. B 11, 1512 (1975).
27. K. Cho, Phys. Rev. B 14, 4463 (1976).
28. J. van W. Morgan and T.N. Morgan, Phys. Rev. B 1, 739 (1970).

29. P.E. Simmonds, H. Venghaus and R. Sooryakumar, Solid State Commun. 43, 311 (1982).
30. G. Davies, E.C. Lightowlers, R. Woolley, R.C. Newman and A.S. Oates, J. Phys. C 17, L499 (1984).
31. T.N. Morgan, Phys. Rev. Lett. 21, 819 (1968).
32. J.A. van Vechten, Phys. Rev. 182, 891 (1969) and Phys. Rev. 187, 1007 (1969).
33. A.M. Stoneham, "Theory of Defects in Solids". (Oxford, 1975).
34. E.E. Haller and L.M. Falicov, Phys. Rev. Lett. 41, 1192 (1978).
35. E.E. Haller, B. Joós and L.M. Falicov, Phys. Rev. B 21, 4729 (1980).
36. K.M. Lee, K.P. O'Donnell, J. Weber, B.C. Cavenett and G.D. Watkins, Phys. Rev. Lett. 48, 37 (1982).

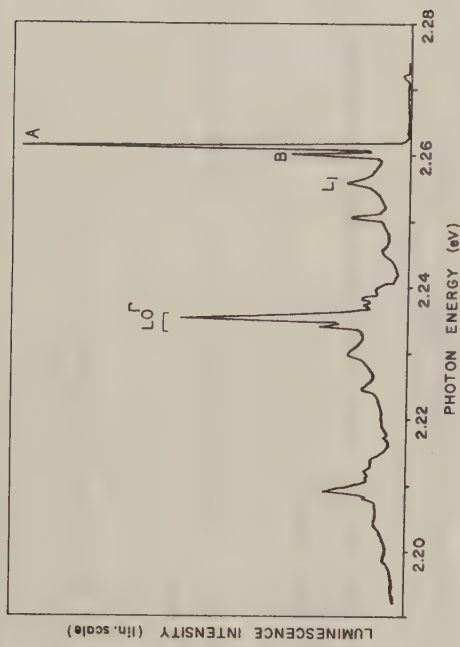


Fig. 1 PL spectrum of the 2.26 eV BE with bandgap excitation. The exciton has two no-phonon lines, the A and B line and a strong phonon wing. The LO as well as a quasi-localized mode, L_1 , are indicated in the figure.

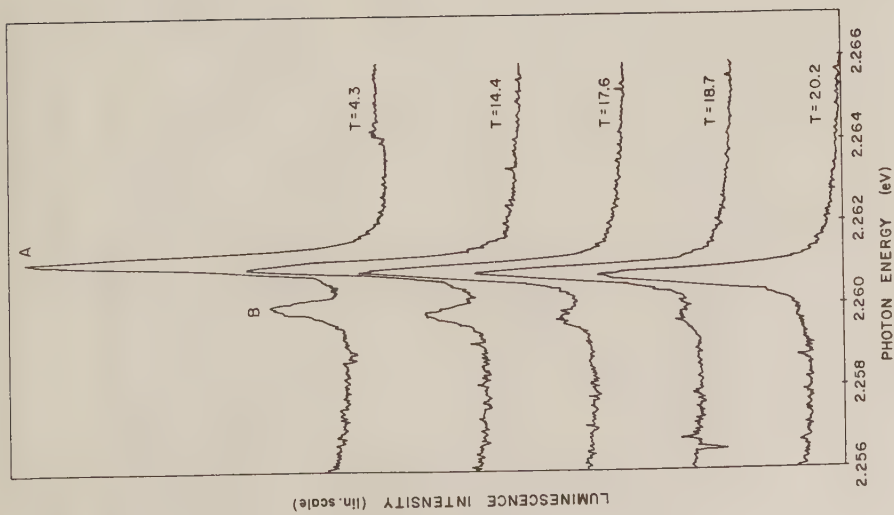


Fig. 2 The PL spectra for the 2.26 eV emission at some different temperatures. The low-energy B line is quenched at higher temperatures, while the A line is still prominent.

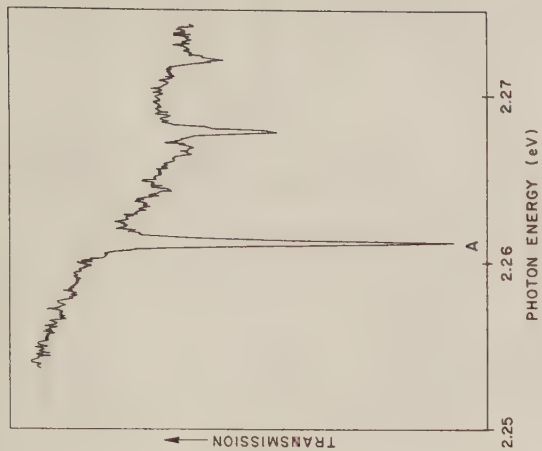


Fig. 3 Transmission spectrum of the 2.26 eV BE showing a strong effect from the A line, while the B line is hardly detectable. Also present is absorption at 2.268 eV from another centre.

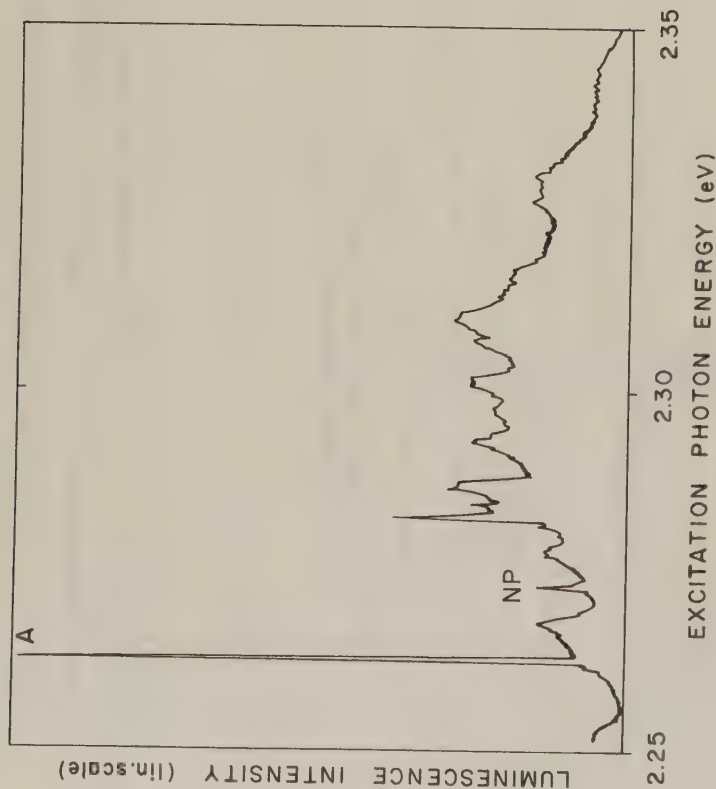


Fig. 4 PLE spectrum of the 2.26 eV bound exciton with detection at the LO replica of the same emission. The A line is strongly observed along with a well-structured phonon band. For phonon energies in comparison with PL measurements, see Table 1. The peak denoted NP is related to a no phonon line of a different centre.

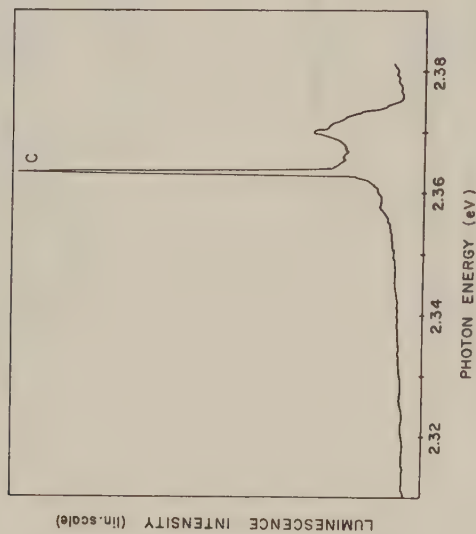


Fig. 5 Excitation spectrum at higher energy than in Fig. 4, with detection in the 2.26 eV BE. A strong excited state, denoted C, is seen.

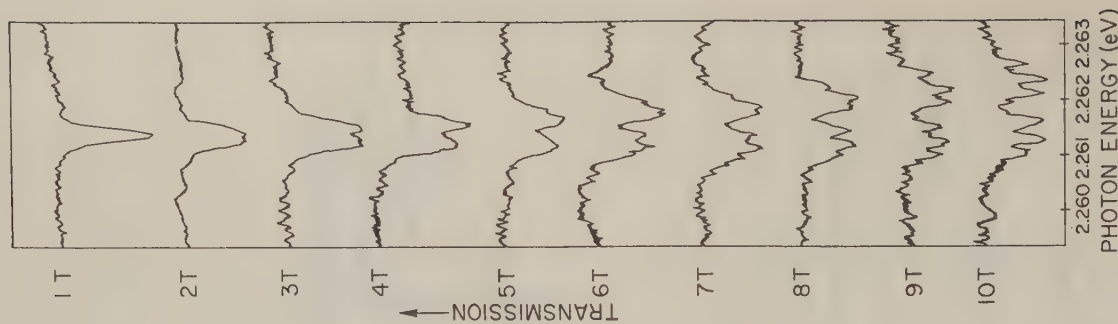


Fig. 6 Transmission spectra of the Cu-related A-line at magnetic fields between 1T and 10T in an arbitrary direction.

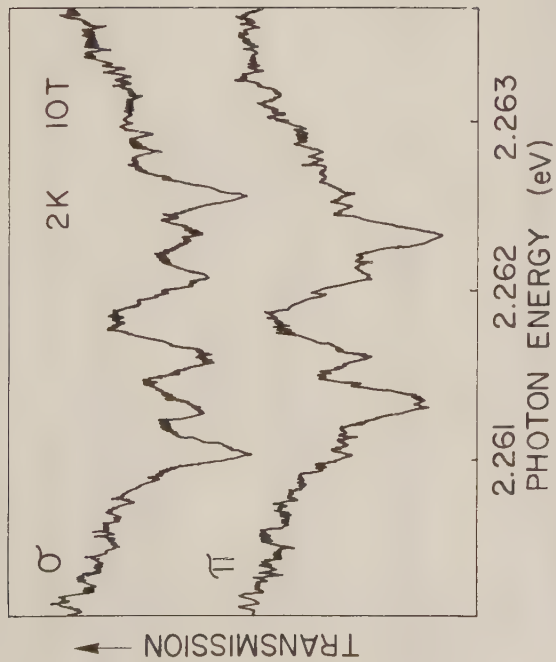


Fig. 7 Polarized transmission spectra at 10T in the Voigt configuration.

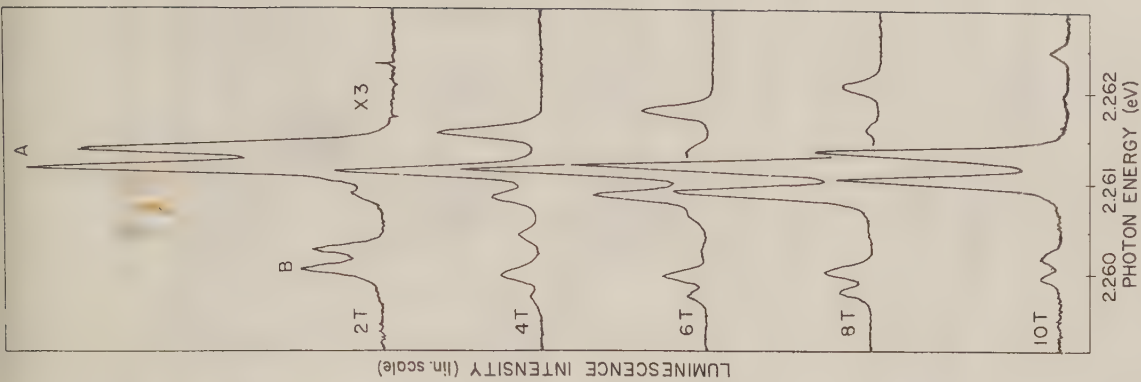


Fig. 8 PL spectra of the Cu-related A and B lines as a function of a magnetic field up to 10T. A very similar magnetic behaviour is observed for the two lines.

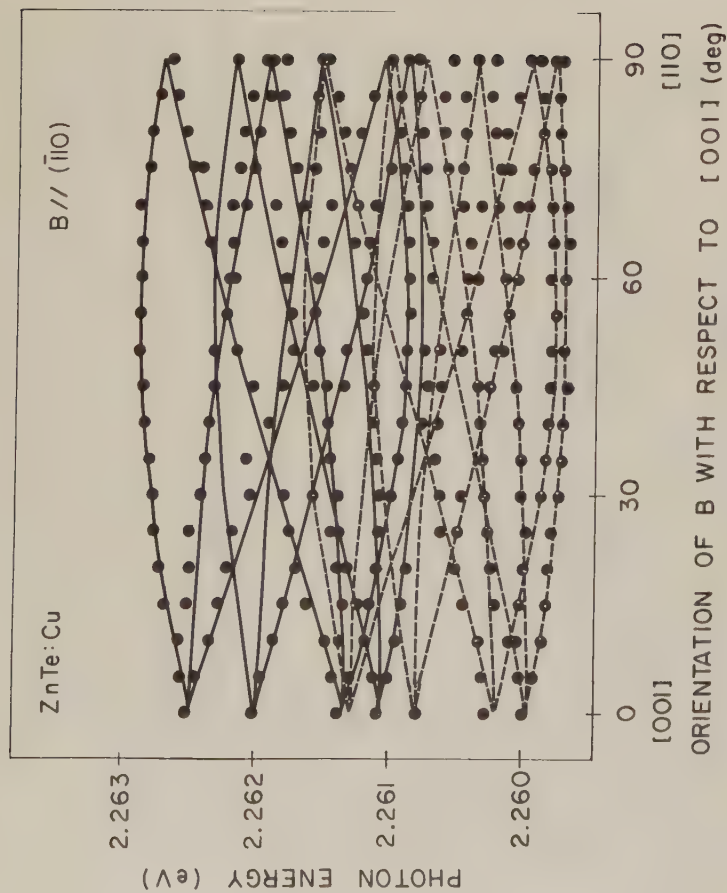


Fig. 9 Angular dependence of the Zeeman split A and B lines at 10T. The crystal was rotated in a $(1\bar{1}0)$ plane. $B // [001]$ is denoted by 0 deg. The dots show experimental points. The solid lines are calculated for the A line and the dashed lines refer to the B line.

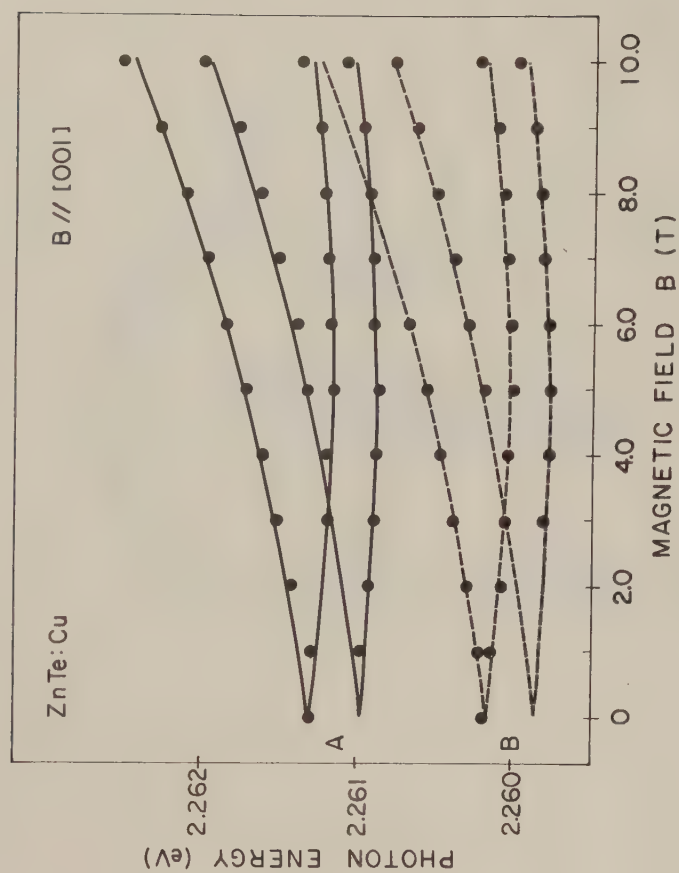


Fig. 10 Fan diagram of the splitting of the A and B lines in magnetic fields between 0T and 10T. Solid lines are calculated positions for the split A line and the dashed lines are corresponding positions for the B line.

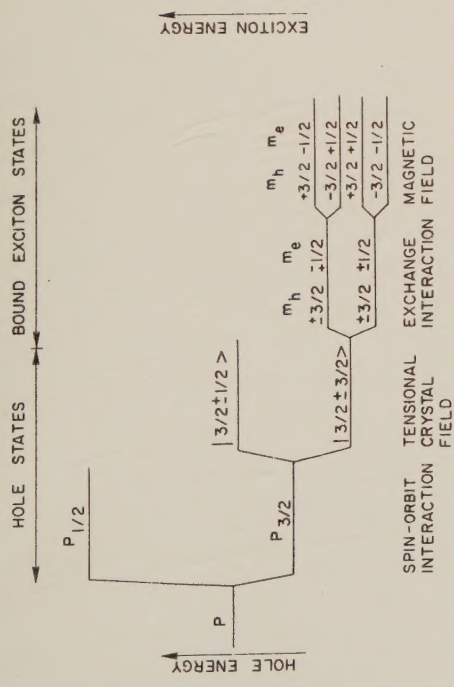


Fig. 11 The electronic structure for an exciton perturbed by a tensional crystal field and a magnetic field.

Spin-orbit interaction splits the p-like hole states into a $p_{1/2}$ and $p_{3/2}$ state with $p_{3/2}$ being lowest in energy. A tensional field further splits the $p_{3/2}$ state into a $|3/2, \pm 1/2\rangle$ state and a $|3/2, \pm 3/2\rangle$ state with the $|3/2, \pm 3/2\rangle$ state having the lowest energy. Introducing an electron gives a further splitting by the exchange interaction indicated in the figure. Finally a magnetic field will give four states with indicated m_h and m_e values.

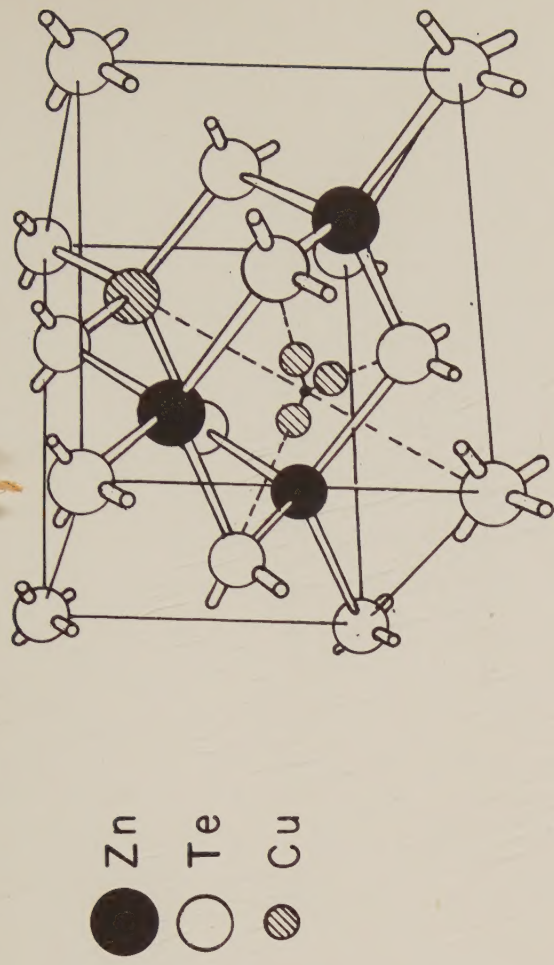
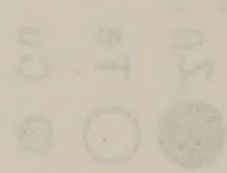


Fig. 12 A model of the suggested identity of the centre studied in this paper. One Cu-atom substitutes on a Zn-site while a second Cu_i has three possible positions. The nearest neighbours are assumed to be Te. The potential barrier between the interstitial positions is suggested to be small giving rise to two nuclear wave functions for the Cu_i -atom having A_1 and E symmetry, respectively.

Figure 1

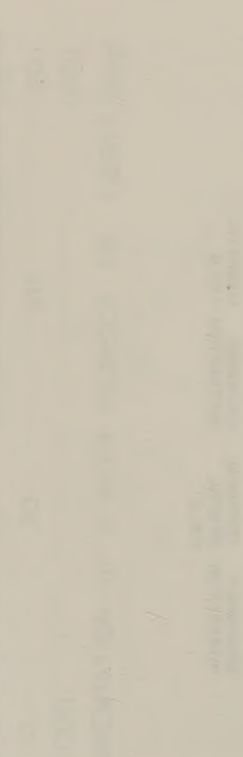
The first part of the paper is devoted to a description of the experimental setup and the results obtained. The second part is devoted to a discussion of the results and the conclusions drawn from them. The third part is devoted to a description of the experimental setup and the results obtained. The fourth part is devoted to a discussion of the results and the conclusions drawn from them.



The diagram illustrates the structure of the network, showing the connections between the different nodes.

Figure 2

The second part of the paper is devoted to a description of the experimental setup and the results obtained. The third part is devoted to a discussion of the results and the conclusions drawn from them. The fourth part is devoted to a description of the experimental setup and the results obtained. The fifth part is devoted to a discussion of the results and the conclusions drawn from them.



The diagram illustrates the structure of the network, showing the connections between the different nodes. The nodes are represented by circles of different sizes and are connected by lines. The diagram illustrates a hierarchical or interconnected structure.

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